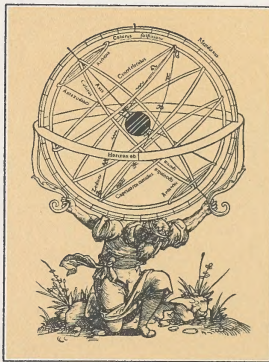


PART - I

(1875)

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**Thomson** (Sir Joseph John) *APPLICATIONS OF DYNAMICS TO PHYSICS AND CHEMISTRY.*  
London, Macmillan, 1888. First edition. 8vo. viii, 312 (2) pp. Original plum-  
coloured cloth, gilt, spine worn. £7.10.0.

J. J.'s second book and very rare. He says in his preface that his methods are analogous  
to those of Prof. Willard Gibbs in his celebrated paper on the *Equilibrium of Heterogenous*  
*Substances.* DAWSON-63



*Prof. John Tyndall, F.R.S.  
from the author.*

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[FROM THE TRANSACTIONS OF THE CONNECTICUT ACADEMY OF ARTS AND SCIENCES.  
VOL. III, PART 1.]

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ON THE EQUILIBRIUM  
OF  
HETEROGENEOUS SUBSTANCES.

FIRST PART.

By J. WILLARD GIBBS,  
PROFESSOR OF MATHEMATICAL PHYSICS IN YALE COLLEGE, NEW HAVEN, CONN.

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ON THE EQUILIBRIUM OF HETEROGENEOUS SUBSTANCES.  
BY J. WILLARD GIBBS.

“Die Energie der Welt ist constant.  
Die Entropie der Welt strebt einem Maximum zu.”  
CLAUSIUS.\*

THE comprehension of the laws which govern any material system is greatly facilitated by considering the energy and entropy of the system in the various states of which it is capable. As the difference of the values of the energy for any two states represents the combined amount of work and heat received or yielded by the system when it is brought from one state to the other, and the difference of entropy is the limit of all the possible values of the integral  $\int \frac{dQ}{t}$ , ( $dQ$  denoting the element of the heat received from external sources, and  $t$  the temperature of the part of the system receiving it,) the varying values of the energy and entropy characterize in all that is essential the effects producible by the system in passing from one state to another. For by mechanical and thermodynamic contrivances, supposed theoretically perfect, any supply of work and heat may be transformed into any other which does not differ from it either in the amount of work and heat taken together or in the value of the integral  $\int \frac{dQ}{t}$ . But it is not only in respect to the external relations of a system that its energy and entropy are of predominant importance. As in the case of simply mechanical systems, (such as are discussed in theoretical mechanics,) which are capable of only one kind of action upon external systems, viz., the performance of mechanical work, the function which expresses the capability of the system for this kind of action also plays the leading part in the theory of equilibrium, the condition of equilibrium being that the variation of this function shall vanish, so in a thermodynamic system, (such as all material systems actually are,) which is capable of two different kinds of action upon external systems, the two functions which express the twofold capabilities of the system afford an almost equally simple criterion of equilibrium.

\*Pogg. Ann. Bd. cxxv (1865), S. 400; or Mechanische Wärmetheorie, Abhand. ix., S. 44.



## CRITERIA OF EQUILIBRIUM AND STABILITY.

The criterion of equilibrium for a material system which is isolated from all external influences may be expressed in either of the following entirely equivalent forms:

I. *For the equilibrium of any isolated system it is necessary and sufficient that in all possible variations of the state of the system which do not alter its energy, the variation of its entropy shall either vanish or be negative.* If  $\varepsilon$  denote the energy, and  $\eta$  the entropy of the system, and we use a subscript letter after a variation to indicate a quantity of which the value is not to be varied, the condition of equilibrium may be written

$$(\delta\eta)_{\varepsilon} \leq 0. \quad (1)$$

II. *For the equilibrium of any isolated system it is necessary and sufficient that in all possible variations in the state of the system which do not alter its entropy, the variation of its energy shall either vanish or be positive.* This condition may be written

$$(\delta\varepsilon)_{\eta} \geq 0. \quad (2)$$

That these two theorems are equivalent will appear from the consideration that it is always possible to increase both the energy and the entropy of the system, or to decrease both together, viz., by imparting heat to any part of the system or by taking it away. For, if condition (1) is not satisfied, there must be some variation in the state of the system for which

$$\delta\eta > 0 \text{ and } \delta\varepsilon = 0;$$

therefore, by diminishing both the energy and the entropy of the system *in its varied state*, we shall obtain a state for which (considered as a variation from the original state)

$$\delta\eta = 0 \text{ and } \delta\varepsilon < 0;$$

therefore condition (2) is not satisfied. Conversely, if condition (2) is not satisfied, there must be a variation in the state of the system for which

$$\delta\varepsilon < 0 \text{ and } \delta\eta = 0;$$

hence there must also be one for which

$$\delta\varepsilon = 0 \text{ and } \delta\eta > 0;$$

therefore condition (1) is not satisfied.

The equations which express the condition of equilibrium, as also its statement in words, are to be interpreted in accordance with the general usage in respect to differential equations, that is, infinitesimals

of higher orders than the first relatively to those which express the amount of change of the system are to be neglected. But to distinguish the different kinds of equilibrium in respect to stability, we must have regard to the absolute values of the variations. We will use  $\Delta$  as the sign of variation in those equations which are to be construed *strictly*, i. e., in which infinitesimals of the higher orders are not to be neglected. With this understanding, we may express the necessary and sufficient conditions of the different kinds of equilibrium as follows;—for stable equilibrium

$$(\Delta\eta)_\varepsilon < 0, \text{ i. e., } (\Delta\varepsilon)_\eta > 0; \quad (3)$$

for neutral equilibrium there must be some variations in the state of the system for which

$$(\Delta\eta)_\varepsilon = 0, \text{ i. e., } (\Delta\varepsilon)_\eta = 0, \quad (4)$$

while in general

$$(\Delta\eta)_\varepsilon \leq 0, \text{ i. e., } (\Delta\varepsilon)_\eta \geq 0; \quad (5)$$

and for unstable equilibrium there must be some variations for which

$$(\Delta\eta)_\varepsilon > 0, \quad (6)$$

i. e., there must be some for which

$$(\Delta\varepsilon)_\eta < 0, \quad (7)$$

while in general

$$(\delta\eta)_\varepsilon \leq 0, \text{ i. e., } (\delta\varepsilon)_\eta \geq 0. \quad (8)$$

In these criteria of equilibrium and stability, account is taken only of *possible* variations. It is necessary to explain in what sense this is to be understood. In the first place, all variations in the state of the system which involve the transportation of any matter through any finite distance are of course to be excluded from consideration, although they may be capable of expression by infinitesimal variations of quantities which perfectly determine the state of the system. For example, if the system contains two masses of the same substance, not in contact, nor connected by other masses consisting of or containing the same substance or its components, an infinitesimal increase of the one mass with an equal decrease of the other is not to be considered as a possible variation in the state of the system. In addition to such cases of essential impossibility, if heat can pass by conduction or radiation from every part of the system to every other, only those variations are to be rejected as impossible, which involve changes which are prevented by passive forces or analogous resistances to change. But, if the system consist of parts between which there is supposed to be no thermal communication, it will be necessary to regard as impossible any diminution of the entropy of any of



these parts, as such a change can not take place without the passage of heat. This limitation may most conveniently be applied to the second of the above forms of the condition of equilibrium, which will then become

$$(\delta\varepsilon)_{\eta', \eta'', \text{etc.}} \geq 0, \quad (9)$$

$\eta', \eta'', \text{etc.}$ , denoting the entropies of the various parts between which there is no communication of heat. When the condition of equilibrium is thus expressed, the limitation in respect to the conduction of heat will need no farther consideration.

In order to apply to any system the criteria of equilibrium which have been given, a knowledge is requisite of its passive forces or resistances to change, in so far, at least, as they are capable of *preventing* change. (Those passive forces which only retard change, like viscosity, need not be considered.) Such properties of a system are in general easily recognized upon the most superficial knowledge of its nature. As examples, we may instance the passive force of friction which prevents sliding when two surfaces of solids are pressed together,—that which prevents the different components of a solid, and sometimes of a fluid, from having different motions one from another,—that resistance to change which sometimes prevents either of two forms of the same substance (simple or compound), which are capable of existing, from passing into the other,—that which prevents the changes in solids which imply plasticity, (in other words, changes of the form to which the solid tends to return,) when the deformation does not exceed certain limits.

It is a characteristic of all these passive resistances that they prevent a certain kind of motion or change, however the initial state of the system may be modified, and to whatever external agencies of force and heat it may be subjected, within limits, it may be, but yet within limits which allow finite variations in the values of all the quantities which express the initial state of the system or the mechanical or thermal influences acting on it, without producing the change in question. The equilibrium which is due to such passive properties is thus widely distinguished from that caused by the balance of the active tendencies of the system, where an external influence, or a change in the initial state, infinitesimal in amount, is sufficient to produce change either in the positive or negative direction. Hence the ease with which these passive resistances are recognized. Only in the case that the state of the system lies so near the limit at which the resistances cease to be operative to prevent change, as to create a

doubt whether the case falls within or without the limit, will a more accurate knowledge of these resistances be necessary.

To establish the validity of the criterion of equilibrium, we will consider first the sufficiency, and afterwards the necessity, of the condition as expressed in either of the two equivalent forms.

In the first place, if the system is in a state in which its entropy is greater than in any other state of the same energy, it is evidently in equilibrium, as any change of state must involve either a decrease of entropy or an increase of energy, which are alike impossible for an isolated system. We may add that this is a case of *stable* equilibrium, as no infinitely small cause (whether relating to a variation of the initial state or to the action of any external bodies) can produce a finite change of state, as this would involve a finite decrease of entropy or increase of energy.

We will next suppose that the system has the greatest entropy consistent with its energy, and therefore the least energy consistent with its entropy, but that there are other states of the same energy and entropy as its actual state. In this case, it is impossible that any motion of masses should take place; for if any of the energy of the system should come to consist of *vis viva* (of sensible motions), a state of the system identical in other respects but without the motion would have less energy and not less entropy, which would be contrary to the supposition. (But we cannot apply this reasoning to the motion within any mass of its different components in different directions, as in diffusion, when the momenta of the components balance one another.) Nor, in the case supposed, can any conduction of heat take place, for this involves an increase of entropy, as heat is only conducted from bodies of higher to those of lower temperature. It is equally impossible that any changes should be produced by the transfer of heat by radiation. The condition which we have supposed is therefore sufficient for equilibrium, so far as the motion of masses and the transfer of heat are concerned, but to show that the same is true in regard to the motions of diffusion and chemical or molecular changes, when these can occur without being accompanied or followed by the motions of masses or the transfer of heat, we must have recourse to considerations of a more general nature. The following considerations seem to justify the belief that the condition is sufficient for equilibrium in every respect.

Let us suppose, in order to test the tenability of such a hypothesis, that a system may have the greatest entropy consistent with its energy without being in equilibrium. In such a case, changes in the



state of the system must take place, but these will necessarily be such that the energy and the entropy will remain unchanged and the system will continue to satisfy the same condition, as initially, of having the greatest entropy consistent with its energy. Let us consider the change which takes place in any time so short that the change may be regarded as uniform in nature throughout that time. This time must be so chosen that the change does not take place in it infinitely slowly, which is always easy, as the change which we suppose to take place cannot be infinitely slow except at particular moments. Now no change whatever in the state of the system, which does not alter the value of the energy, and which commences with the same state in which the system was supposed at the commencement of the short time considered, will cause an increase of entropy. Hence, it will generally be possible by some slight variation in the circumstances of the case to make all changes in the state of the system like or nearly like that which is supposed actually to occur, and not involving a change of energy, to involve a necessary decrease of entropy, which would render any such change impossible. This variation may be in the values of the variables which determine the state of the system, or in the values of the constants which determine the nature of the system, or in the form of the functions which express its laws,—only there must be nothing in the system as modified which is thermodynamically impossible. For example, we might suppose temperature or pressure to be varied, or the composition of the different bodies in the system, or, if no small variations which could be actually realized would produce the required result, we might suppose the properties themselves of the substances to undergo variation, subject to the general laws of matter. If, then, there is any tendency toward change in the system as first supposed, it is a tendency which can be entirely checked by an infinitesimal variation in the circumstances of the case. As this supposition cannot be allowed, we must believe that a system is always in equilibrium when it has the greatest entropy consistent with its energy, or, in other words, when it has the least energy consistent with its entropy.

The same considerations will evidently apply to any case in which a system is in such a state that  $\Delta\eta \leq 0$  for any possible infinitesimal variation of the state for which  $\Delta\varepsilon = 0$ , even if the entropy is not the least of which the system is capable with the same energy. (The term *possible* has here the meaning previously defined, and the character  $\Delta$  is used, as before, to denote that the equations are to be

construed strictly, i. e., without neglect of the infinitesimals of the higher orders.)

The only case in which the sufficiency of the condition of equilibrium which has been given remains to be proved is that in which in our notation  $\delta\eta \leq 0$  for all possible variations not affecting the energy, but for some of these variations  $\Delta\eta > 0$ , that is, when the entropy has in some respects the characteristics of a minimum. In this case the considerations adduced in the last paragraph will not apply without modification, as the change of state may be infinitely slow at first, and it is only in the initial state that the condition  $\delta\eta_e \leq 0$  holds true. But the differential coefficients of all orders of the quantities which determine the state of the system, taken with respect of the time, must be functions of these same quantities. None of these differential coefficients can have any value other than 0, for the state of the system for which  $\delta\eta_e \leq 0$ . For otherwise, as it would generally be possible, as before, by some infinitely small modification of the case, to render impossible any change like or nearly like that which might be supposed to occur, this infinitely small modification of the case would make a finite difference in the value of the differential coefficients which had before the finite values, or in some of lower orders, which is contrary to that continuity which we have reason to expect. Such considerations seem to justify us in regarding such a state as we are discussing as one of theoretical equilibrium; although as the equilibrium is evidently unstable, it cannot be realized.

We have still to prove that the condition enunciated is in every case necessary for equilibrium. It is evidently so in all cases in which the active tendencies of the system are so balanced that changes of every kind, except those excluded in the statement of the condition of equilibrium, can take place *reversibly*, (i. e., both in the positive and the negative direction,) in states of the system differing infinitely little from the state in question. In this case, we may omit the sign of inequality and write as the condition of such a state of equilibrium

$$(\delta\eta)_e = 0, \quad \text{i. e.,} \quad (\delta\varepsilon)_\eta = 0 \quad (10)$$

But to prove that the condition previously enunciated is in every case necessary, it must be shown that whenever an isolated system remains without change, if there is any infinitesimal variation in its state, not involving a finite change of position of any (even an infinitesimal part) of its matter, which would diminish its energy by a



quantity which is not infinitely small relatively to the variations of the quantities which determine the state of the system, without altering its entropy,—or, if the system has thermally isolated parts, without altering the entropy of any such part,—this variation involves changes in the system which are prevented by its passive forces or analogous resistances to change. Now, as the described variation in the state of the system diminishes its energy without altering its entropy, it must be regarded as theoretically possible to produce that variation by some process, perhaps a very indirect one, so as to gain a certain amount of work (above all expended on the system). Hence we may conclude that the active forces or tendencies of the system favor the variation in question, and that equilibrium cannot subsist unless the variation is prevented by passive forces.

The preceding considerations will suffice, it is believed, to establish the validity of the criterion of equilibrium which has been given. The criteria of stability may readily be deduced from that of equilibrium. We will now proceed to apply these principles to systems consisting of heterogeneous substances and deduce the special laws which apply to different classes of phenomena. For this purpose we shall use the second form of the criterion of equilibrium, both because it admits more readily the introduction of the condition that there shall be no thermal communication between the different parts of the system, and because it is more convenient, as respects the form of the general equations relating to equilibrium, to make the entropy one of the independent variables which determine the state of the system, than to make the energy one of these variables.

THE CONDITIONS OF EQUILIBRIUM FOR HETEROGENEOUS MASSES IN  
CONTACT WHEN UNINFLUENCED BY GRAVITY, ELECTRICITY, DISTORTION  
OF THE SOLID MASSES, OR CAPILLARY TENSIONS.

In order to arrive as directly as possible at the most characteristic and essential laws of chemical equilibrium, we will first give our attention to a case of the simplest kind. We will examine the conditions of equilibrium of a mass of matter of various kinds enclosed in a rigid and fixed envelop, which is impermeable to and unalterable by any of the substances enclosed, and perfectly non-conducting to heat. We will suppose that the case is not complicated by the action of gravity, or by any electrical influences, and that in the solid portions of the mass the pressure is the same in every direction.

We will farther simplify the problem by supposing that the variations of the parts of the energy and entropy which depend upon the surfaces separating heterogeneous masses are so small in comparison with the variations of the parts of the energy and entropy which depend upon the quantities of these masses, that the former may be neglected by the side of the latter; in other words, we will exclude the considerations which belong to the theory of capillarity.

It will be observed that the supposition of a rigid and non-conducting envelop enclosing the mass under discussion involves no real loss of generality, for if any mass of matter is in equilibrium, it would also be so, if the whole or any part of it were enclosed in an envelop as supposed; therefore the conditions of equilibrium for a mass thus enclosed are the general conditions which must always be satisfied in case of equilibrium. As for the other suppositions which have been made, all the circumstances and considerations which are here excluded will afterward be made the subject of special discussion.

*Conditions relating to the Equilibrium between the initially existing Homogeneous Parts of the given Mass.*

Let us first consider the energy of any homogeneous part of the given mass, and its variation for any possible variation in the composition and state of this part. (By *homogeneous* is meant that the part in question is uniform throughout, not only in chemical composition, but also in physical state.) If we consider the amount and kind of matter in this homogeneous mass as fixed, its energy  $\varepsilon$  is a function of its entropy  $\eta$ , and its volume  $v$ , and the differentials of these quantities are subject to the relation

$$d\varepsilon = t d\eta - p dv, \quad (11)$$

$t$  denoting the (absolute) temperature of the mass, and  $p$  its pressure. For  $t d\eta$  is the heat received, and  $p dv$  the work done, by the mass during its change of state. But if we consider the matter in the mass as variable, and write  $m_1, m_2, \dots m_n$  for the quantities of the various substances  $S_1, S_2, \dots S_n$  of which the mass is composed,  $\varepsilon$  will evidently be a function of  $\eta, v, m_1, m_2, \dots m_n$ , and we shall have for the complete value of the differential of  $\varepsilon$

$$d\varepsilon = t d\eta - p dv + \mu_1 dm_1 + \mu_2 dm_2 \dots + \mu_n dm_n, \quad (12)$$

$\mu_1, \mu_2, \dots \mu_n$  denoting the differential coefficients of  $\varepsilon$  taken with respect to  $m_1, m_2, \dots m_n$ .

The substances  $S_1, S_2, \dots S_n$  of which we consider the mass composed, must of course be such that the values of the differen-



tials  $dm_1, dm_2, \dots dm_n$  shall be independent, and shall express every possible variation in the composition of the homogeneous mass considered, including those produced by the absorption of substances different from any initially present. It may therefore be necessary to have terms in the equation relating to component substances which do not initially occur in the homogeneous mass considered, provided, of course, that these substances, or their components, are to be found in some part of the whole given mass.

If the conditions mentioned are satisfied, the choice of the substances which we are to regard as the components of the mass considered, may be determined entirely by convenience, and independently of any theory in regard to the internal constitution of the mass. The number of components will sometimes be greater, and sometimes less, than the number of chemical elements present. For example, in considering the equilibrium in a vessel containing water and free hydrogen and oxygen, we should be obliged to recognize three components in the gaseous part. But in considering the equilibrium of dilute sulphuric acid with the vapor which it yields, we should have only two components to consider in the liquid mass, sulphuric acid (anhydrous, or of any particular degree of concentration) and (additional) water. If, however, we are considering sulphuric acid in a state of maximum concentration in connection with substances which might possibly afford water to the acid, it must be noticed that the condition of the independence of the differentials will require that we consider the acid in the state of maximum concentration as one of the components. The quantity of this component will then be capable of variation both in the positive and in the negative sense, while the quantity of the other component can increase but cannot decrease below the value 0.

For brevity's sake, we may call a substance  $S_a$  an *actual component* of any homogeneous mass, to denote that the quantity  $m_a$  of that substance in the given mass may be either increased or diminished (although we may have so chosen the other component substances that  $m_a = 0$ ); and we may call a substance  $S_b$  a *possible component* to denote that it may be combined with, but cannot be subtracted from the homogeneous mass in question. In this case, as we have seen in the above example, we must so choose the component substances that  $m_b = 0$ .

The units by which we measure the substances of which we regard the given mass as composed may each be chosen independently. To fix our ideas for the purpose of a general discussion, we may suppose

all substances measured by weight or mass. Yet in special cases, it may be more convenient to adopt chemical equivalents as the units of the component substances.

It may be observed that it is not necessary for the validity of equation (12) that the variations of nature and state of the mass to which the equation refers should be such as do not disturb its homogeneity, provided that in all parts of the mass the variations of nature and state are infinitely small. For, if this last condition be not violated, an equation like (12) is certainly valid for all the infinitesimal parts of the (initially) homogeneous mass; i. e., if we write  $D\varepsilon$ ,  $D\eta$ , etc., for the energy, entropy, etc., of any infinitesimal part,

$$dD\varepsilon = t dD\eta - p dDv + \mu_1 dDm_1 + \mu_2 dDm_2 \dots + \mu_n dDm_n, \quad (13)$$

whence we may derive equation (12) by integrating for the whole initially homogeneous mass.

We will now suppose that the whole mass is divided into parts so that each part is homogeneous, and consider such variations in the energy of the system as are due to variations in the composition and state of the several parts remaining (at least approximately) homogeneous, and together occupying the whole space within the envelop. We will at first suppose the case to be such that the component substances are the same for each of the parts, each of the substances  $S_1, S_2, \dots S_n$  being an actual component of each part. If we distinguish the letters referring to the different parts by accents, the variation in the energy of the system may be expressed by  $\delta\varepsilon' + \delta\varepsilon'' + \text{etc.}$ , and the general condition of equilibrium requires that

$$\delta\varepsilon' + \delta\varepsilon'' + \text{etc.} \geq 0 \quad (14)$$

for all variations which do not conflict with the *equations of condition*. These equations must express that the entropy of the whole given mass does not vary, nor its volume, nor the total quantities of any of the substances  $S_1, S_2, \dots S_n$ . We will suppose that there are no other equations of condition. It will then be necessary for equilibrium that

$$\begin{aligned} t' \delta\eta' - p' \delta v' + \mu_1' \delta m_1' + \mu_2' \delta m_2' \dots + \mu_n' \delta m_n' \\ + t'' \delta\eta'' - p'' \delta v'' + \mu_1'' \delta m_1'' + \mu_2'' \delta m_2'' \dots + \mu_n'' \delta m_n'' \\ + \text{etc.} \geq 0 \end{aligned} \quad (15)$$

for any values of the variations for which

$$\delta\eta' + \delta\eta'' + \delta\eta''' + \text{etc.} = 0, \quad (16)$$

$$\delta v' + \delta v'' + \delta v''' + \text{etc.} = 0, \quad (17)$$



$$\left. \begin{aligned} \delta m_1' + \delta m_1'' + \delta m_1''' + \text{etc.} &= 0, \\ \delta m_2' + \delta m_2'' + \delta m_2''' + \text{etc.} &= 0, \\ \text{and } \delta m_n' + \delta m_n'' + \delta m_n''' + \text{etc.} &= 0. \end{aligned} \right\} \quad (18)$$

For this it is evidently necessary and sufficient that

$$t' = t'' = t''' = \text{etc.} \quad (19)$$

$$p' = p'' = p''' = \text{etc.} \quad (20)$$

$$\left. \begin{aligned} \mu_1' &= \mu_1'' = \mu_1''' = \text{etc.} \\ \mu_2' &= \mu_2'' = \mu_2''' = \text{etc.} \\ \mu_n' &= \mu_n'' = \mu_n''' = \text{etc.} \end{aligned} \right\} \quad (21)$$

Equations (19) and (20) express the conditions of thermal and mechanical equilibrium, viz., that the temperature and the pressure must be constant throughout the whole mass. In equations (21) we have the conditions characteristic of chemical equilibrium. If we call a quantity  $\mu_s$ , as defined by such an equation as (12), the *potential* for the substance  $S_s$  in the homogeneous mass considered, these conditions may be expressed as follows:

*The potential for each component substance must be constant throughout the whole mass.*

It will be remembered that we have supposed that there is no restriction upon the freedom of motion or combination of the component substances, and that each is an actual component of all parts of the given mass.

The state of the whole mass will be completely determined (if we regard as immaterial the position and form of the various homogeneous parts of which it is composed), when the values are determined of the quantities of which the variations occur in (15). The number of these quantities, which we may call the independent variables, is evidently  $(n+2)\nu$ ,  $\nu$  denoting the number of homogeneous parts into which the whole mass is divided. All the quantities which occur in (19), (20), (21), are functions of these variables, and may be regarded as known functions, if the energy of each part is known as a function of its entropy, volume, and the quantities of its components. (See eq. (12).) Therefore, equations (19), (20), (21), may be regarded as  $(\nu-1)(n+2)$  independent equations between the independent variables. The volume of the whole mass and the total quantities of the various substances being known afford  $n+1$  additional equations. If we also know the total energy of the given mass, or its total entropy, we will have as many equations as there are independent variables.

But if any of the substances  $S_1, S_2 \dots S_n$  are only possible components of some parts of the given mass, the variation  $\delta m$  of the quantity of such a substance in such a part cannot have a negative value, so that the general condition of equilibrium (15) does not require that the potential for that substance in that part should be equal to the potential for the same substance in the parts of which it is an actual component, but only that it shall not be less. In this case instead of (21) we may write

$$\left. \begin{array}{l} \mu_1 = M_1 \\ \text{for all parts of which } S_1 \text{ is an actual component, and} \\ \mu_1 \geq M_1 \\ \text{for all parts of which } S_1 \text{ is a possible (but not actual) com-} \\ \text{ponent,} \\ \mu_2 = M_2 \\ \text{for all parts of which } S_2 \text{ is an actual component, and} \\ \mu_2 \geq M_2 \\ \text{for all parts of which } S_2 \text{ is a possible (but not actual) com-} \\ \text{ponent,} \\ \text{etc.,} \end{array} \right\} \quad (22)$$

$M_1, M_2$ , etc., denoting constants of which the value is only determined by these equations.

If we now suppose that the components (actual or possible) of the various homogeneous parts of the given mass are not the same, the result will be of the same character as before, provided that all the different components are *independent*, (i. e., that no one can be made out of the others,) so that the total quantity of each component is fixed. The general condition of equilibrium (15) and the equations of condition (16), (17), (18) will require no change, except that, if any of the substances  $S_1, S_2 \dots S_n$  is not a component (actual or possible) of any part, the term  $\mu \delta m$  for that substance and part will be wanting in the former, and the  $\delta m$  in the latter. This will require no change in the form of the particular conditions of equilibrium as expressed by (19), (20), (22); but the number of single conditions contained in (22) is of course less than if all the component substances were components of all the parts. Whenever, therefore, each of the different homogeneous parts of the given mass may be regarded as composed of some or of all of the same set of substances, no one of which can be formed out of the others, the condition which (with equality of temperature and pressure) is necessary and sufficient for equilibrium between the different parts of the given mass may be expressed as follows:



The potential for each of the component substances must have a constant value in all parts of the given mass of which that substance is an actual component, and have a value not less than this in all parts of which it is a possible component.

The number of equations afforded by these conditions, after elimination of  $M_1, M_2, \dots M_n$ , will be less than  $(n + 2)(\nu - 1)$  by the number of terms in (15) in which the variation of the form  $\delta m$  is either necessarily nothing or incapable of a negative value. The number of variables to be determined is diminished by the same number, or, if we choose, we may write an equation of the form  $m = 0$  for each of these terms. But when the substance is a possible component of the part concerned, there will also be a condition (expressed by  $\geq$ ) to show whether the supposition that the substance is not an actual component is consistent with equilibrium.

We will now suppose that the substances  $S_1, S_2, \dots S_n$  are not all independent of each other, i. e., that some of them can be formed out of others. We will first consider a very simple case. Let  $S_3$  be composed of  $S_1$  and  $S_2$  combined in the ratio of  $a$  to  $b$ ,  $S_1$  and  $S_2$  occurring as actual components in some parts of the given mass, and  $S_3$  in other parts, which do not contain  $S_1$  and  $S_2$  as separately variable components. The general condition of equilibrium will still have the form of (15) with certain of the terms of the form  $\mu \delta m$  omitted. It may be written more briefly [(23)

$\sum (t \delta \eta) - \sum (p \delta v) + \sum (\mu_1 \delta m_1) + \sum (\mu_2 \delta m_2) \dots + \sum (\mu_n \delta m_n) \geq 0$ , the sign  $\sum$  denoting summation in regard to the different parts of the given mass. But instead of the three equations of condition,

$$\sum \delta m_1 = 0, \quad \sum \delta m_2 = 0, \quad \sum \delta m_3 = 0, \quad (24)$$

we shall have the two,

$$\left. \begin{aligned} \sum \delta m_1 + \frac{a}{a+b} \sum \delta m_3 &= 0, \\ \sum \delta m_2 + \frac{b}{a+b} \sum \delta m_3 &= 0. \end{aligned} \right\} \quad (25)$$

The other equations of condition,

$$\sum \delta \eta = 0, \quad \sum \delta v = 0, \quad \sum \delta m_4 = 0, \quad \text{etc.}, \quad (26)$$

will remain unchanged. Now as all values of the variations which satisfy equations (24) will also satisfy equations (25), it is evident that all the particular conditions of equilibrium which we have already deduced, (19), (20), (22), are necessary in this case also. When these are satisfied, the general condition (23) reduces to

$$M_1 \sum \delta m_1 + M_2 \sum \delta m_2 + M_3 \sum \delta m_3 \geq 0. \quad (27)$$

For, although it may be that  $\mu_1'$ , for example, is greater than  $M_1$ , yet it can only be so when the following  $\delta m_1'$  is incapable of a negative value. Hence, if (27) is satisfied, (23) must also be. Again, if (23) is satisfied, (27) must also be satisfied, so long as the variation of the quantity of every substance has the value 0 in all the parts of which it is not an actual component. But as this limitation does not affect the range of the possible values of  $\sum \delta m_1$ ,  $\sum \delta m_2$ , and  $\sum \delta m_3$ , it may be disregarded. Therefore the conditions (23) and (27) are entirely equivalent, when (19), (20), (22) are satisfied. Now, by means of the equations of condition (25), we may eliminate  $\sum \delta m_1$  and  $\sum \delta m_2$  from (27), which becomes

$$-a M_1 \sum \delta m_3 - b M_2 \sum \delta m_3 + (a+b) M_3 \sum \delta m_3 \geq 0, \quad (28)$$

i. e., as the value of  $\sum \delta m_3$  may be either positive or negative,

$$a M_1 + b M_2 = (a+b) M_3, \quad (29)$$

which is the additional condition of equilibrium which is necessary in this case.

The relations between the component substances may be less simple than in this case, but in any case they will only affect the equations of condition, and these may always be found without difficulty, and will enable us to eliminate from the general condition of equilibrium as many variations as there are equations of condition, after which the coefficients of the remaining variations may be set equal to zero, except the coefficients of variations which are incapable of negative values, which coefficients must be equal to or greater than zero. It will be easy to perform these operations in each particular case, but it may be interesting to see the form of the resultant equations in general.

We will suppose that the various homogeneous parts are considered as having in all  $n$  components,  $S_1, S_2, \dots, S_n$ , and that there is no restriction upon their freedom of motion and combination. But we will so far limit the generality of the problem as to suppose that each of these components is an actual component of some part of the given mass.\* If some of these components can be formed out of others, all such relations can be expressed by equations such as

$$\alpha \mathfrak{S}_a + \beta \mathfrak{S}_b + \text{etc.} = \kappa \mathfrak{S}_k + \lambda \mathfrak{S}_l + \text{etc.} \quad (30)$$

where  $\mathfrak{S}_a, \mathfrak{S}_b, \mathfrak{S}_k$ , etc. denote the units of the substances  $S_a, S_b, S_k$ , etc.,

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\* When we come to seek the conditions of equilibrium relating to the formation of masses unlike any previously existing, we shall take up *de novo* the whole problem of the equilibrium of heterogeneous masses enclosed in a non-conducting envelop, and give it a more general treatment, which will be free from this limitation.

(that is, of certain of the substances  $S_1, S_2, \dots S_n$ ) and  $\alpha, \beta, \kappa$ , etc. denote numbers. These are not, it will be observed, equations between abstract quantities, but the sign  $=$  denotes qualitative as well as quantitative equivalence. We will suppose that there are  $r$  independent equations of this character. The equations of condition relating to the component substances may easily be derived from these equations, but it will not be necessary to consider them particularly. It is evident that they will be satisfied by any values of the variations which satisfy equations (18); hence, the particular conditions of equilibrium (19), (20), (22) must be necessary in this case, and, if these are satisfied, the general equation of equilibrium (15) or (23) will reduce to

$$M_1 \geq \delta m_1 + M_2 \geq \delta m_2 \dots + M_n \geq \delta m_n \geq 0. \quad (31)$$

This will appear from the same considerations which were used in regard to equations (23) and (27). Now it is evidently possible to give to  $\geq \delta m_a, \geq \delta m_b, \geq \delta m_k$ , etc. values proportional to  $\alpha, \beta, -\kappa$ , etc. in equation (30), and also the same values taken negatively, making  $\geq \delta m = 0$  in each of the other terms; therefore

$$\alpha M_a + \beta M_b + \text{etc.} \dots - \kappa M_k - \lambda M_l - \text{etc.} = 0, \quad (32)$$

or,

$$\alpha M_a + \beta M_b + \text{etc.} = \kappa M_k + \lambda M_l + \text{etc.} \quad (33)$$

It will be observed that this equation has the same form and coefficients as equation (30),  $M$  taking the place of  $\mathfrak{S}$ . It is evident that there must be a similar condition of equilibrium for every one of the  $r$  equations of which (30) is an example, which may be obtained simply by changing  $\mathfrak{S}$  in these equations into  $M$ . When these conditions are satisfied, (31) will be satisfied with any possible values of  $\geq \delta m_1, \geq \delta m_2, \dots \geq \delta m_n$ . For no values of these quantities are possible, except such that the equation

$$(\geq \delta m_1) \mathfrak{S}_1 + (\geq \delta m_2) \mathfrak{S}_2 \dots + (\geq \delta m_n) \mathfrak{S}_n = 0 \quad (34)$$

after the substitution of these values, can be derived from the  $r$  equations like (30), by the ordinary processes of the reduction of linear equations. Therefore, on account of the correspondence between (31) and (34), and between the  $r$  equations like (33) and the  $r$  equations like (30), the conditions obtained by giving any possible values to the variations in (31) may also be derived from the  $r$  equations like (33); that is, the condition (31) is satisfied, if the  $r$  equations like (33) are satisfied. Therefore the  $r$  equations like (33) are with (19), (20), and (22) the equivalent of the general condition (15) or (23).



For determining the state of a given mass when in equilibrium and having a given volume and given energy or entropy, the condition of equilibrium affords an additional equation corresponding to each of the  $r$  independent relations between the  $n$  component substances. But the equations which express our knowledge of the matter in the given mass will be correspondingly diminished, being  $n - r$  in number, like the equations of condition relating to the quantities of the component substances, which may be derived from the former by differentiation.

*Conditions relating to the possible Formation of Masses Unlike any Previously Existing.*

The variations which we have hitherto considered do not embrace every possible infinitesimal variation in the state of the given mass, so that the particular conditions already formed, although always necessary for equilibrium (when there are no other equations of condition than such as we have supposed), are not always sufficient. For, besides the infinitesimal variations in the state and composition of different parts of the given mass, infinitesimal masses may be formed entirely different in state and composition from any initially existing. Such parts of the whole mass in its varied state as cannot be regarded as parts of the initially existing mass which have been infinitesimally varied in state and composition, we will call *new parts*. These will necessarily be infinitely small. As it is more convenient to regard a vacuum as a limiting case of extreme rarefaction than to give a special consideration to the possible formation of empty spaces within the given mass, the term *new parts* will be used to include any empty spaces which may be formed, when such have not existed initially. We will use  $D\varepsilon$ ,  $D\eta$ ,  $Dv$ ,  $Dm_1$ ,  $Dm_2$ , . . .  $Dm_n$  to denote the infinitesimal energy, entropy, and volume of any one of these new parts, and the infinitesimal quantities of its components. The component substances  $S_1$ ,  $S_2$ , . . .  $S_n$  must now be taken to include not only the independently variable components (actual or possible) of all parts of the given mass as initially existing, but also the components of all the new parts, the possible formation of which we have to consider. The character  $\delta$  will be used as before to express the infinitesimal variations of the quantities relating to those parts which are only infinitesimally varied in state and composition, and which for distinction we will call *original parts*, including under this term the empty spaces, if such exist initially, within the envelop bounding the system. As we may divide the given mass into as many parts as we choose, and as not only the

initial boundaries, but also the movements of these boundaries during any variation in the state of the system are arbitrary, we may so define the parts which we have called original, that we may consider them as initially homogeneous and remaining so, and as initially constituting the whole system.

The most general value of the energy of the whole system is evidently

$$\Sigma \delta \varepsilon + \Sigma D\varepsilon, \quad (35)$$

the first summation relating to all the original parts, and the second to all the new parts. (Throughout the discussion of this problem, the letter  $\delta$  or  $D$  following  $\Sigma$  will sufficiently indicate whether the summation relates to the original or to the new parts.) Therefore the general condition of equilibrium is

$$\Sigma \delta \varepsilon + \Sigma D\varepsilon \geq 0, \quad (36)$$

or, if we substitute the value of  $\delta \varepsilon$  taken from equation (12), [(37)

$$\Sigma D\varepsilon + \Sigma (t\delta\eta) - \Sigma (p\delta v) + \Sigma (\mu_1\delta m_1) + \Sigma (\mu_2\delta m_2) \dots + \Sigma (\mu_n\delta m_n) \geq 0.$$

If any of the substances  $S_1, S_2, \dots S_n$  can be formed out of others, we will suppose, as before (see page 122), that such relations are expressed by equations between the units of the different substances. Let these be

$$\left. \begin{array}{l} a_1 \mathfrak{S}_1 + a_2 \mathfrak{S}_2 \dots + a_n \mathfrak{S}_n = 0 \\ b_1 \mathfrak{S}_1 + b_2 \mathfrak{S}_2 \dots + b_n \mathfrak{S}_n = 0 \\ \text{etc.} \end{array} \right\} r \text{ equations. } (38)$$

The equations of condition will be (if there is no restriction upon the freedom of motion and composition of the components)

$$\Sigma \delta \eta + \Sigma D\eta = 0, \quad (39)$$

$$\Sigma \delta v + \Sigma Dv = 0, \quad (40)$$

and  $n - r$  equations of the form

$$\left. \begin{array}{l} h_1 (\Sigma \delta m_1 + \Sigma Dm_1) + h_2 (\Sigma \delta m_2 + \Sigma Dm_2) \dots \\ \quad \quad \quad + h_n (\Sigma \delta m_n + \Sigma Dm_n) = 0 \\ i_1 (\Sigma \delta m_1 + \Sigma Dm_1) + i_2 (\Sigma \delta m_2 + \Sigma Dm_2) \dots \\ \quad \quad \quad + i_n (\Sigma \delta m_n + \Sigma Dm_n) = 0 \\ \text{etc.} \end{array} \right\} (41)^*$$

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\* In regard to the relation between the coefficients in (41) and those in (38), the reader will easily convince himself that the coefficients of any one of equations (41) are such as would satisfy all the equations (38) if substituted for  $S_1, S_2, \dots S_n$ ; and that this is the only condition which these coefficients must satisfy, except that the  $n - r$  sets of coefficients shall be independent, i. e., shall be such as to form independent equations; and that this relation between the coefficients of the two sets of equations is a reciprocal one.

Now, using Lagrange's "method of multipliers,"\* we will subtract  $T' (\sum \delta \eta + \sum D\eta) - P (\sum \delta v + \sum Dv)$  from the first member of the general condition of equilibrium (37),  $T$  and  $P$  being constants of which the value is as yet arbitrary. We might proceed in the same way with the remaining equations of condition, but we may obtain the same result more simply in another way. We will first observe that

$$(\sum \delta m_1 + \sum Dm_1) \mathfrak{S}_1 + (\sum \delta m_2 + \sum Dm_2) \mathfrak{S}_2 \dots + (\sum \delta m_n + \sum Dm_n) \mathfrak{S}_n = 0, \quad (42)$$

which equation would hold identically for any possible values of the quantities in the parentheses, if for  $r$  of the letters  $\mathfrak{S}_1, \mathfrak{S}_2, \dots \mathfrak{S}_n$  were substituted their values in terms of the others as derived from equations (38). (Although  $\mathfrak{S}_1, \mathfrak{S}_2, \dots \mathfrak{S}_n$  do not represent abstract quantities, yet the operations necessary for the reduction of linear equations are evidently applicable to equations (38).) Therefore, equation (42) will hold true if for  $\mathfrak{S}_1, \mathfrak{S}_2, \dots \mathfrak{S}_n$  we substitute  $n$  numbers which satisfy equations (38). Let  $M_1, M_2, \dots M_n$  be such numbers, i. e., let

$$\left. \begin{aligned} a_1 M_1 + a_2 M_2 \dots + a_n M_n &= 0, \\ b_1 M_1 + b_2 M_2 \dots + b_n M_n &= 0, \\ &\text{etc.} \end{aligned} \right\} r \text{ equations, } (43)$$

then

$$M_1 (\sum \delta m_1 + \sum Dm_1) + M_2 (\sum \delta m_2 + \sum Dm_2) \dots + M_n (\sum \delta m_n + \sum Dm_n) = 0. \quad (44)$$

This expression, in which the values of  $n - r$  of the constants  $M_1, M_2, \dots M_n$  are still arbitrary, we will also subtract from the first member of the general condition of equilibrium (37), which will then become

$$\begin{aligned} \sum D\varepsilon + \sum (t \delta \eta) - \sum (p \delta v) + \sum (\mu_1 \delta m_1) \dots + \sum (\mu_n \delta m_n) \\ - T \sum \delta \eta + P \sum \delta v - M_1 \sum \delta m_1 \dots + M_n \sum \delta m_n \\ - T \sum D\eta + P \sum Dv - M_1 \sum Dm_1 \dots - M_n \sum Dm_n \geq 0. \end{aligned} \quad (45)$$

That is, having assigned to  $T, P, M_1, M_2, \dots M_n$  any values consistent with (43), we may assert that it is necessary and sufficient for equilibrium that (45) shall hold true for any variations in the state of the system consistent with the equations of condition (39), (40), (41). But it will always be possible, in case of equilibrium, to assign such values to  $T, P, M_1, M_2, \dots M_n$ , without violating equations (43),

\* On account of the sign  $\geq$  in (37), and because some of the variations are incapable of negative values, the successive steps in the reasoning will be developed at greater length than would be otherwise necessary.



that (45) shall hold true for all variations in the state of the system and in the quantities of the various substances composing it, even though these variations are not consistent with the equations of condition (39), (40), (41). For, when it is not possible to do this, it must be possible by applying (45) to variations in the system not necessarily restricted by the equations of condition (39), (40), (41) to obtain conditions in regard to  $T$ ,  $P$ ,  $M_1$ ,  $M_2$ , . . .  $M_n$ , some of which will be inconsistent with others or with equations (43). These conditions we will represent by

$$A \geq 0, \quad B \geq 0, \quad \text{etc.}, \quad (46)$$

$A$ ,  $B$ , etc. being linear functions of  $T$ ,  $P$ ,  $M_1$ ,  $M_2$ , . . .  $M_n$ . Then it will be possible to deduce from these conditions a single condition of the form

$$\alpha A + \beta B + \text{etc.} \geq 0, \quad (47)$$

$\alpha$ ,  $\beta$ , etc. being positive constants, which cannot hold true consistently with equations (43). But it is evident from the form of (47) that, like any of the conditions (46), it could have been obtained directly from (45) by applying this formula to a certain change in the system (perhaps not restricted by the equations of condition (39), (40), (41)). Now as (47) cannot hold true consistently with eqs. (43), it is evident, in the first place, that it cannot contain  $T$  or  $P$ , therefore in the change in the system just mentioned (for which (45) reduces to (47))

$$\sum \delta \eta + \sum D\eta = 0, \quad \text{and} \quad \sum \delta v + \sum Dv = 0,$$

so that the equations of condition (39) and (40) are satisfied. Again, for the same reason, the homogeneous function of the first degree of  $M_1$ ,  $M_2$ , . . .  $M_n$  in (47) must be one of which the value is fixed by eqs. (43). But the value thus fixed can only be zero, as is evident from the form of these equations. Therefore

$$\begin{aligned} (\sum \delta m_1 + \sum Dm_1) M_1 + (\sum \delta m_2 + \sum Dm_2) M_2 \dots \\ + (\sum \delta m_n + \sum Dm_n) M_n = 0 \end{aligned} \quad (48)$$

for any values of  $M_1$ ,  $M_2$  . . .  $M_n$  which satisfy eqs. (43), and therefore

$$\begin{aligned} (\sum \delta m_1 + \sum Dm_1) \mathfrak{S}_1 + (\sum \delta m_2 + \sum Dm_2) \mathfrak{S}_2 \dots \\ + (\sum \delta m_n + \sum Dm_n) \mathfrak{S}_n = 0 \end{aligned} \quad (49)$$

for any numerical values of  $\mathfrak{S}_1$ ,  $\mathfrak{S}_2$ , . . .  $\mathfrak{S}_n$  which satisfy eqs. (38). This equation (49) will therefore hold true, if for  $r$  of the letters  $\mathfrak{S}$ ,  $\mathfrak{S}_2$ , . . .  $\mathfrak{S}_n$  we substitute their values in terms of the others taken from eqs. (38), and therefore it will hold true when we use

$\mathfrak{S}_1, \mathfrak{S}_2, \dots \mathfrak{S}_n$ , as before, to denote the units of the various components. Thus understood, the equation expresses that the values of the quantities in the parentheses are such as are consistent with the equations of condition (41). The change in the system, therefore, which we are considering, is not one which violates any of the equations of condition, and as (45) does not hold true for this change, and for all values of  $T, P, M_1, M_2, \dots M_n$  which are consistent with eqs. (43), the state of the system cannot be one of equilibrium. Therefore it is necessary, and it is evidently sufficient for equilibrium, that it shall be possible to assign to  $T, P, M_1, M_2, \dots M_n$  such values, consistent with eqs. (43), that the condition (45) shall hold true for any change in the system irrespective of the equations of condition (39), (40), (41).

For this it is necessary and sufficient that

$$t = T, \quad p = P, \quad (50)$$

$$\mu_1 \delta m_1 \geq M_1 \delta m_1, \quad \mu_2 \delta m_2 \geq M_2 \delta m_2, \dots \mu_n \delta m_n \geq M_n \delta m_n \quad (51)$$

for each of the *original parts* as previously defined, and that

$$D\varepsilon - T D\eta + P Dv - M_1 Dm_1 - M_2 Dm_2 \dots - M_n Dm_n \geq 0, \quad (52)$$

for each of the *new parts* as previously defined. If to these conditions we add equations (43), we may treat  $T, P, M_1, M_2, \dots M_n$  simply as unknown quantities to be eliminated.

In regard to conditions (51), it will be observed that if a substance,  $S_1$ , is an actual component of the part of the given mass distinguished by a single accent,  $\delta m_1'$  may be either positive or negative, and we shall have  $\mu_1' = M_1$ ; but if  $S_1$  is only a possible component of that part,  $\delta m_1'$  will be incapable of a negative value, and we will have  $\mu_1' \geq M_1$ .

The formulæ (50), (51), and (43) express the same particular conditions of equilibrium which we have before obtained by a less general process. It remains to discuss (52). This formula must hold true of any infinitesimal mass in the system in its varied state which is not approximately homogeneous with any of the surrounding masses, the expressions  $D\varepsilon, D\eta, Dv, Dm_1, Dm_2, \dots Dm_n$  denoting the energy, entropy, and volume of this infinitesimal mass, and the quantities of the substances  $S_1, S_2, \dots S_n$  which we regard as composing it, (not necessarily as *independently* variable components). If there is more than one way in which this mass may be considered as composed of these substances, we may choose whichever is most convenient. Indeed it follows directly from the relations existing between  $M_1, M_2, \dots$  and  $M_n$  that the result would be the same in

any case. Now, if we assume that the values of  $D\varepsilon$ ,  $D\eta$ ,  $Dv$ ,  $Dm_1$ ,  $Dm_2$ , . . .  $Dm_n$  are proportional to the values of  $\varepsilon$ ,  $\eta$ ,  $v$ ,  $m_1$ ,  $m_2$ , . . .  $m_n$  for any large homogeneous mass of similar composition, and of the same temperature and pressure, the condition is equivalent to this, that

$$\varepsilon - T\eta + Pv - M_1 m_1 - M_2 m_2 \dots - M_n m_n \geq 0 \quad (53)$$

for any large homogeneous body which can be formed out of the substances  $S_1$ ,  $S_2$  . . .  $S_n$ .

But the validity of this last transformation cannot be admitted without considerable limitation. It is assumed that the relation between the energy, entropy, volume, and the quantities of the different components of a very small mass surrounded by substances of different composition and state is the same as if the mass in question formed a part of a large homogeneous body. We started, indeed, with the assumption that we might neglect the part of the energy, etc., depending upon the surfaces separating heterogeneous masses. Now, in many cases, and for many purposes, as, in general, when the masses are large, such an assumption is quite legitimate, but in the case of these masses which are formed within or among substances of different nature or state, and which at their first formation must be infinitely small, the same assumption is evidently entirely inadmissible, as the surfaces must be regarded as infinitely large in proportion to the masses. We shall see hereafter what modifications are necessary in our formulæ in order to include the parts of the energy, etc., which are due to the surfaces, but this will be on the assumption, which is usual in the theory of capillarity, that the radius of curvature of the surfaces is large in proportion to the radius of sensible molecular action, and also to the thickness of the lamina of matter at the surface which is not (sensibly) homogeneous in all respects with either of the masses which it separates. But although the formulæ thus modified will apply with sensible accuracy to masses (occurring within masses of a different nature) much smaller than if the terms relating to the surfaces were omitted, yet their failure when applied to masses infinitely small in all their dimensions is not less absolute.

Considerations like the foregoing might render doubtful the validity even of (52) as the necessary and sufficient condition of equilibrium in regard to the formation of masses not approximately homogeneous with those previously existing, when the conditions of equilibrium between the latter are satisfied, unless it is shown that in establishing this formula there have been no quantities neglected relating to the



mutual action of the new and the original parts, which can affect the result. It will be easy to give such a meaning to the expressions  $D\varepsilon$ ,  $D\eta$ ,  $Dv$ ,  $Dm_1$ ,  $Dm_2$ , . . .  $Dm_n$  that this shall be evidently the case. It will be observed that the quantities represented by these expressions have not been perfectly defined. In the first place, we have no right to assume the existence of any surface of absolute discontinuity to divide the new parts from the original, so that the position given to the dividing surface is to a certain extent arbitrary. Even if the surface separating the masses were determined, the energy to be attributed to the masses separated would be partly arbitrary, since a part of the total energy depends upon the mutual action of the two masses. We ought perhaps to consider the case the same in regard to the entropy, although the entropy of a system never depends upon the mutual relations of parts at sensible distances from one another. Now the condition (52) will be valid if the quantities  $D\varepsilon$ ,  $D\eta$ ,  $Dv$ ,  $Dm_1$ ,  $Dm_2$  . . .  $Dm_n$  are so defined that none of the assumptions which have been made, tacitly or otherwise, relating to the formation of these new parts, shall be violated. These assumptions are the following:—that the relation between the variations of the energy, entropy, volume, etc., of any of the original parts is not affected by the vicinity of the new parts; and that the energy, entropy, volume, etc., of the system in its varied state are correctly represented by the sums of the energies, entropies, volumes, etc., of the various parts (original and new), so far at least as any of these quantities are determined or affected by the formation of the new parts. We will suppose  $D\varepsilon$ ,  $D\eta$ ,  $Dv$ ,  $Dm_1$ ,  $Dm_2$  . . .  $Dm_n$  to be so defined that these conditions shall not be violated. This may be done in various ways. We may suppose that the position of the surfaces separating the new and the original parts has been fixed in any suitable way. This will determine the space and the matter belonging to the parts separated. If this does not determine the division of the entropy, we may suppose this determined in any suitable arbitrary way. Thus we may suppose the total energy in and about any new part to be so distributed that equation (12) as applied to the original parts shall not be violated by the formation of the new parts. Or, it may seem more simple to suppose that the imaginary surface which divides any new part from the original is so placed as to include all the matter which is affected by the vicinity of the new formation, so that the part or parts which we regard as original may be left homogeneous in the strictest sense, including uniform *densities of energy and entropy*, up to the very

bounding surface. The homogeneity of the new parts is of no consequence, as we have made no assumption in that respect. It may be doubtful whether we can consider the new parts, *as thus bounded*, to be infinitely small even in their earliest stages of development. But if they are not infinitely small, the only way in which this can affect the validity of our formulæ will be that in virtue of the equations of condition, i. e., in virtue of the evident necessities of the case, finite variations of the energy, entropy, volume, etc., of the original parts will be caused, to which it might seem that equation (12) would not apply. But if the nature and state of the mass be not varied, equation (12) will hold true of finite differences. (This appears at once, if we integrate the equation under the above limitation.) Hence, the equation will hold true for finite differences, provided that the nature and state of the mass be infinitely little varied. For the differences may be considered as made up of two parts, of which the first are for a constant nature and state of the mass, and the second are infinitely small. We may therefore regard the new parts to be bounded as supposed without prejudice to the validity of any of our results.

The condition (52) understood in either of these ways (or in others which will suggest themselves to the reader) will have a perfectly definite meaning, and will be valid as the necessary and sufficient condition of equilibrium in regard to the formation of new parts, when the conditions of equilibrium in regard to the original parts, (50), (51), and (43), are satisfied.

In regard to the condition (53), it may be shown that with (50), (51), and (43) it is always sufficient for equilibrium. To prove this, it is only necessary to show that when (50), (51), and (43) are satisfied, and (52) is not, (53) will also not be satisfied.

We will first observe that an expression of the form

$$-\varepsilon + T\eta - Pv + M_1 m_1 + M_2 m_2 \dots + M_n m_n \quad (54)$$

denotes the work obtainable by the formation (by a reversible process) of a body of which  $\varepsilon$ ,  $\eta$ ,  $v$ ,  $m_1$ ,  $m_2$ , . . .  $m_n$  are the energy, entropy, volume, and the quantities of the components, within a medium having the pressure  $P$ , the temperature  $T$ , and the potentials  $M_1$ ,  $M_2$ , . . .  $M_n$ . (The medium is supposed so large that its properties are not sensibly altered in any part by the formation of the body.) For  $\varepsilon$  is the energy of the body formed, and the remaining terms represent (as may be seen by applying equation (12) to the medium) the decrease of the energy of the medium, if, after the

formation of the body, the joint entropy of the medium and the body, their joint volumes and joint quantities of matter, were the same as the entropy, etc., of the medium before the formation of the body. This consideration may convince us that for any given finite values of  $v$  and of  $T, P, M_1$ , etc. this expression cannot be infinite when  $\varepsilon, \eta, m_1$ , etc. are determined by any real body, whether homogeneous or not, (but of the given volume), even when  $T, P, M_1$ , etc. do not represent the values of the temperature, pressure, and potentials of any real substance. (If the substances  $S_1, S_2, \dots S_n$  are all actual components of any homogeneous part of the system of which the equilibrium is discussed, that part will afford an example of a body having the temperature, pressure, and potentials of the medium supposed.)

Now by integrating equation (12) on the supposition that the nature and state of the mass considered remain unchanged, we obtain the equation

$$\varepsilon = t\eta - pv + \mu_1 m_1 + \mu_2 m_2 \dots + \mu_n m_n \quad (55)$$

which will hold true of any homogeneous mass whatever. Therefore for any one of the original parts, by (50) and (51),

$$\varepsilon - T\eta + Pv - M_1 m_1 - M_2 m_2 \dots - M_n m_n = 0. \quad (56)$$

If the condition (52) is not satisfied in regard to all possible new parts, let  $N$  be a new part occurring in an original part  $O$ , for which the condition is not satisfied. It is evident that the value of the expression

$$\varepsilon - T\eta + Pv - M_1 m_1 - M_2 m_2 \dots - M_n m_n \quad (57)$$

applied to a mass like  $O$  including some very small masses like  $N$ , will be negative, and will decrease if the number of these masses like  $N$  is increased, until there remains within the whole mass no portion of any sensible size without these masses like  $N$ , which, it will be remembered, have no sensible size. But it cannot decrease without limit, as the value of (54) cannot become infinite. Now we need not inquire whether the least value of (57) (for constant values of  $T, P, M_1, M_2, \dots M_n$ ) would be obtained by excluding entirely the mass like  $O$ , and filling the whole space considered with masses like  $N$ , or whether a certain mixture would give a smaller value,—it is certain that the least possible value of (57) per unit of volume, and that a negative value, will be realized by a mass having a certain homogeneity. If the new part  $N$  for which the condition (52) is not satisfied occurs between two different original parts  $O'$  and  $O''$ , the argument need not be essentially varied. We may consider the



value of (57) for a body consisting of masses like  $O'$  and  $O''$  separated by a lamina  $N$ . This value may be decreased by increasing the extent of this lamina, which may be done within a given volume by giving it a convoluted form; and it will be evident, as before, that the least possible value of (57) will be for a homogeneous mass, and that the value will be negative. And such a mass will be not merely an ideal combination, but a body capable of existing, for as the expression (57) has for this mass in the state considered its least possible value per unit of volume, the energy of the mass included in a unit of volume is the least possible for the same matter with the same entropy and volume,—hence, if confined in a non-conducting vessel, it will be in a state of not unstable equilibrium. Therefore when (50), (51), and (43) are satisfied, if the condition (52) is not satisfied in regard to all possible new parts, there will be some homogeneous body which can be formed out of the substances  $S_1, S_2, \dots S_n$  which will not satisfy condition (53).

Therefore, if the initially existing masses satisfy the conditions (50), (51), and (43), and condition (53) is satisfied by every homogeneous body which can be formed out of the given matter, there will be equilibrium.

On the other hand, (53) is not a necessary condition of equilibrium. For we may easily conceive that the condition (52) shall hold true (for any very small formations within or between any of the given masses), while the condition (53) is not satisfied (for all large masses formed of the given matter), and experience shows that this is very often the case. Supersaturated solutions, superheated water, etc., are familiar examples. Such an equilibrium will, however, be *practically* unstable. By this is meant that, although, strictly speaking, an infinitely small disturbance or change may not be sufficient to destroy the equilibrium, yet a very small change in the initial state, perhaps a circumstance which entirely escapes our powers of perception, will be sufficient to do so. The presence of a small portion of the substance for which the condition (53) does not hold true, is sufficient to produce this result, when this substance forms a variable component of the original homogeneous masses. In other cases, when, if the new substances are formed at all, different kinds must be formed simultaneously, the initial presence of the different kinds, and that in immediate proximity, may be necessary.

It will be observed, that from (56) and (53) we can at once obtain (50) and (51), viz., by applying (53) to bodies differing infinitely little from the various homogeneous parts of the given mass. There-

fore, the condition (56) (relating to the various homogeneous parts of the given mass) and (53) (relating to any bodies which can be formed of the given matter) with (43) are always sufficient for equilibrium, and always necessary for an equilibrium which shall be practically stable. And, if we choose, we may get rid of limitation in regard to equations (43). For, if we compare these equations with (38), it is easy to see that it is always immaterial, in applying the tests (56) and (53) to any body, how we consider it to be composed. Hence, in applying these tests, we may consider all bodies to be composed of the *ultimate* components of the given mass. Then the terms in (56) and (53) which relate to other components than these will vanish, and we need not regard the equations (43). Such of the constants  $M_1, M_2, \dots, M_n$  as relate to the ultimate components, may be regarded, like  $T$  and  $P$ , as unknown quantities subject only to the conditions (56) and (53).

These two conditions, which are sufficient for equilibrium and necessary for a practically stable equilibrium, may be united in one, viz., (if we choose the ultimate components of the given mass for the component substances to which  $m_1, m_2, \dots, m_n$  relate) that it shall be possible to give such values to the constants  $T, P, M_1, M_2, \dots, M_n$  in the expression (57) that the value of the expression for each of the homogeneous parts of the mass in question shall be as small as for any body whatever made of the same components.

#### *Effect of Solidity of any Part of the given Mass.*

If any of the homogeneous masses of which the equilibrium is in question are solid, it will evidently be proper to treat the proportion of their components as invariable in the application of the criterion of equilibrium, even in the case of *compounds of variable proportions*, i. e., even when bodies can exist which are compounded in proportions infinitesimally varied from those of the solids considered. (Those solids which are capable of absorbing fluids form of course an exception, so far as their fluid components are concerned.) It is true that a solid may be increased by the formation of new solid matter on the surface where it meets a fluid, which is not homogeneous with the previously existing solid, but such a deposit will properly be treated as a distinct part of the system, (viz., as one of the parts which we have called *new*). Yet it is worthy of notice that if a homogeneous solid which is a compound of variable proportions is in contact and equilibrium with a fluid, and the actual components of the solid (considered as of variable composition) are also actual com-

ponents of the fluid, and the condition (53) is satisfied in regard to all bodies which can be formed out of the actual components of the fluid, (which will always be the case unless the fluid is practically unstable,) all the conditions will hold true of the solid, which would be necessary for equilibrium if it were fluid.

This follows directly from the principles stated on the preceding pages. For in this case the value of (57) will be zero as determined either for the solid or for the fluid considered with reference to their ultimate components, and will not be negative for any body whatever which can be formed of these components; and these conditions are sufficient for equilibrium independently of the solidity of one of the masses. Yet the point is perhaps of sufficient importance to demand a more detailed consideration.

Let  $S_a, \dots S_g$  be the actual components of the solid, and  $S_h, \dots S_k$  its possible components (which occur as actual components in the fluid); then, considering the proportion of the components of the solid as variable, we shall have for this body by equation (12)

$$d\varepsilon' = t d\eta' - p' dv' + \mu_a' dm_a' \dots + \mu_g' dm_g' \\ + \mu_h' dm_h' \dots + \mu_k' dm_k'. \quad (58)$$

By this equation the potentials  $\mu_a' \dots \mu_k'$  are perfectly defined. But the differentials  $dm_a' \dots dm_k'$ , considered as independent, evidently express variations which are not *possible* in the sense required in the criterion of equilibrium. We might, however, introduce them into the general condition of equilibrium, if we should express the dependence between them by the proper equations of condition. But it will be more in accordance with our method hitherto, if we consider the solid to have only a single independently variable component  $S_x$ , of which the nature is represented by the solid itself. We may then write

$$\delta\varepsilon' = t' \delta\eta' - p' \delta v' + \mu_x' \delta m_x'. \quad (59)$$

In regard to the relation of the potential  $\mu_x'$  to the potentials occurring in equation (58) it will be observed, that as we have by integration of (58) and (59)

$$\varepsilon' = t' \eta' - p' v' + \mu_a' m_a' \dots + \mu_g' m_g', \quad (60)$$

$$\text{and} \quad \varepsilon' = t' \eta' - p' v' + \mu_x' m_x'; \quad (61)$$

$$\text{therefore} \quad \mu_x' m_x' = \mu_a' m_a' \dots + \mu_g' m_g'. \quad (62)$$

Now, if the fluid has besides  $S_a \dots S_g$  and  $S_h \dots S_k$  the actual components  $S_l \dots S_n$ , we may write for the fluid



$$\delta\varepsilon'' = t'' \delta\eta'' - p'' \delta v'' + \mu_a'' \delta m_a'' \dots + \mu_g'' \delta m_g'' \\ + \mu_h'' \delta m_h'' \dots + \mu_k'' \delta m_k'' + \mu_l'' \delta m_l'' \dots + \mu_n'' \delta m_n'', \quad (63)$$

and as by supposition

$$m_x' \mathfrak{S}_x = m_a' \mathfrak{S}_a \dots + m_g' \mathfrak{S}_g \quad (64)$$

equations (43), (50), and (51) will give in this case on elimination of the constants  $T, P$ , etc.,

$$t' = t'', \quad p' = p'', \quad (65)$$

and

$$m_x' \mu_x' = m_a' \mu_a'' \dots + m_g' \mu_g''. \quad (66)$$

Equations (65) and (66) may be regarded as expressing the conditions of equilibrium between the solid and the fluid. The last condition may also, in virtue of (62), be expressed by the equation

$$m_a' \mu_a' \dots + m_g' \mu_g' = m_a' \mu_a'' \dots + m_g' \mu_g''. \quad (67)$$

But if condition (53) holds true of all bodies which can be formed of  $S_a \dots S_g, S_h, \dots S_k, S_l \dots S_n$ , we may write for all such bodies

$$\varepsilon - t'' \eta + p'' v - \mu_a'' m_a \dots - \mu_g'' m_g - \mu_h'' m_h \\ \dots - \mu_k'' m_k - \mu_l'' m_l \dots - \mu_n'' m_n \geq 0. \quad (68)$$

(In applying this formula to various bodies, it is to be observed that only the values of the unaccented letters are to be determined by the different bodies to which it is applied, the values of the accented letters being already determined by the given fluid.) Now, by (60), (65), and (67), the value of the first member of this condition is zero when applied to the solid in its given state. As the condition must hold true of a body differing infinitesimally from the solid, we shall have

$$d\varepsilon' - t'' d\eta' + p'' dv' - \mu_a'' dm_a' \dots - \mu_g'' dm_g' \\ - \mu_h'' dm_h' \dots - \mu_k'' dm_k' \geq 0, \quad (69)$$

or, by equations (58) and (65),

$$(\mu_a' - \mu_a'') dm_a' \dots + (\mu_g' - \mu_g'') dm_g' \\ + (\mu_h' - \mu_h'') dm_h' \dots + (\mu_k' - \mu_k'') dm_k' \geq 0. \quad (70)$$

Therefore, as these differentials are all independent,

$$\mu_a' = \mu_a'', \dots \mu_g' = \mu_g'', \quad \mu_h' \geq \mu_h'', \dots \mu_k' \geq \mu_k''; \quad (71)$$

which with (65) are evidently the same conditions which we would have obtained if we had neglected the fact of the solidity of one of the masses.

We have supposed the solid to be homogeneous. But it is evident that in any case the above conditions must hold for every separate point where the solid meets the fluid. Hence, the temperature and pressure and the potentials for all the actual components of the solid must have a constant value in the solid at the surface where it meets the fluid. Now, these quantities are determined by the nature and state of the solid, and exceed in number the independent variations of which its nature and state are capable. Hence, if we reject as improbable the supposition that the nature or state of a body can vary without affecting the value of any of these quantities, we may conclude that a solid which varies (continuously) in nature or state at its surface cannot be in equilibrium with a stable fluid which contains, as independently variable components, the variable components of the solid. (There may be, however, in equilibrium with the same stable fluid, a *finite* number of different solid bodies, composed of the variable components of the fluid, and having their nature and state completely determined by the fluid.)\*

#### *Effect of Additional Equations of Condition.*

As the equations of condition, of which we have made use, are such as always apply to matter enclosed in a rigid, impermeable, and non-conducting envelop, the particular conditions of equilibrium which we have found will always be sufficient for equilibrium. But the number of conditions necessary for equilibrium, will be diminished, in a case otherwise the same, as the number of equations of condition is increased. Yet the problem of equilibrium which has been treated will sufficiently indicate the method to be pursued in all cases and the general nature of the results.

It will be observed that the position of the various homogeneous parts of the given mass, which is otherwise immaterial, may determine the existence of certain equations of condition. Thus, when different parts of the system in which a certain substance is a variable component are entirely separated from one another by parts of which this substance is not a component, the quantity of this substance will be invariable for each of the parts of the system which are thus separated, which will be easily expressed by equations of condition. Other equations of condition may arise from the passive forces (or resistances to change) inherent in the given masses. In the prob-

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\* The solid has been considered as subject only to isotropic stresses. The effect of other stresses will be considered hereafter.

lem which we are next to consider there are equations of condition due to a cause of a different nature.

*Effect of a Diaphragm (Equilibrium of Osmotic Forces).*

If the given mass, enclosed as before, is divided into two parts, each of which is homogeneous and fluid, by a diaphragm which is capable of supporting an excess of pressure on either side, and is permeable to some of the components and impermeable to others, we shall have the equations of condition

$$\delta\eta' + \delta\eta'' = 0, \quad (72)$$

$$\delta v' = 0, \quad \delta v'' = 0, \quad (73)$$

and for the components which cannot pass the diaphragm

$$\delta m_a' = 0, \quad \delta m_a'' = 0, \quad \delta m_b' = 0, \quad \delta m_b'' = 0, \quad \text{etc.}, \quad (74)$$

and for those which can

$$\delta m_h' + \delta m_h'' = 0, \quad \delta m_i' + \delta m_i'' = 0, \quad \text{etc.} \quad (75)$$

With these equations of condition, the general condition of equilibrium (see (15)) will give the following particular conditions:

$$t' = t'', \quad (76)$$

and for the components which can pass the diaphragm, if actual components of both masses,

$$\mu_h' = \mu_h'', \quad \mu_i' = \mu_i'', \quad \text{etc.}, \quad (77)$$

but not

$$p' = p'',$$

nor

$$\mu_a' = \mu_a'', \quad \mu_b' = \mu_b'', \quad \text{etc.}$$

Again, if the diaphragm is permeable to the components in certain proportions only, or in proportions not entirely determined yet subject to certain conditions, these conditions may be expressed by equations of condition, which will be linear equations between  $\delta m_1'$ ,  $\delta m_2'$ , etc., and if these be known the deduction of the particular conditions of equilibrium will present no difficulties. We will however observe that if the components  $S_1$ ,  $S_2$ , etc. (being actual components on each side) can pass the diaphragm simultaneously in the proportions  $a_1$ ,  $a_2$ , etc. (without other resistances than such as vanish with the velocity of the current), values proportional to  $a_1$ ,  $a_2$ , etc. are possible for  $\delta m_1'$ ,  $\delta m_2'$ , etc. in the general condition of equilibrium,  $\delta m_1''$ ,  $\delta m_2''$ , etc. having the same values taken negatively, so that we shall have for one particular condition of equilibrium

$$a_1 \mu_1' + a_2 \mu_2' + \text{etc.} = a_1 \mu_1'' + a_2 \mu_2'' + \text{etc.} \quad (78)$$

There will evidently be as many independent equations of this form



as there are independent combinations of the elements which can pass the diaphragm.

These conditions of equilibrium do not of course depend in any way upon the supposition that the volume of each fluid mass is kept constant, if the diaphragm is in any case supposed immovable. In fact, we may easily obtain the same conditions of equilibrium, if we suppose the volumes variable. In this case, as the equilibrium must be preserved by forces acting upon the external surfaces of the fluids, the variation of the energy of the sources of these forces must appear in the general condition of equilibrium, which will be

$$\delta\epsilon' + \delta\epsilon'' + P' \delta v' + P'' \delta v'' \geq 0, \quad (79)$$

$P'$  and  $P''$  denoting the external forces per unit of area. (Compare (14).) From this condition we may evidently derive the same internal conditions of equilibrium as before, and in addition the external conditions

$$p' = P', \quad p'' = P''. \quad (80)$$

In the preceding paragraphs it is assumed that the permeability of the diaphragm is perfect, and its impermeability absolute, i. e., that it offers no resistance to the passage of the components of the fluids in certain proportions, except such as vanishes with the velocity, and that in other proportions the components cannot pass at all. How far these conditions are satisfied in any particular case is of course to be determined by experiment.

If the diaphragm is permeable to all the  $n$  components without restriction, the temperature and the potentials for all the components must be the same on both sides. Now, as one may easily convince himself, a mass having  $n$  components is capable of only  $n+1$  independent variations in nature and state. Hence, if the fluid on one side of the diaphragm remains without change, that on the other side cannot (in general) vary in nature or state. Yet the pressure will not necessarily be the same on both sides. For, although the pressure is a function of the temperature and the  $n$  potentials, it may be a many-valued function (or any one of several functions) of these variables. But when the pressures are different on the two sides, the fluid which has the less pressure will be *practically unstable*, in the sense in which the term has been used on page 133. For

$$\epsilon'' - t'' \eta'' + p'' v'' - \mu_1'' m_1'' - \mu_2'' m_2'' \dots - \mu_n'' m_n'' = 0, \quad (81)$$

as appears from equation (12) if integrated on the supposition that the nature and state of the mass remain unchanged. Therefore, if  $p' < p''$  while  $t' = t''$ ,  $\mu_1' = \mu_1''$ , etc.,

$$\varepsilon'' - t' \eta'' + p' v'' - \mu_1' m_1'' - \mu_2' m_2'' \dots - \mu_n' m_n'' < 0. \quad (82)$$

This relation indicates the instability of the fluid to which the single accents refer. (See page 133.)

But independently of any assumption in regard to the permeability of the diaphragm, the following relation will hold true in any case in which each of the two fluid masses may be regarded as uniform throughout in nature and state. Let the character  $\nu$  be used with the variables which express the nature, state, and quantity of the fluids to denote the increments of the values of these quantities actually occurring in a time either finite or infinitesimal. Then, as the heat received by the two masses cannot exceed  $t' D\eta' + t'' D\eta''$ , and as the increase of their energy is equal to the difference of the heat they receive and the work they do,

$$D\varepsilon' + D\varepsilon'' \leq t' D\eta' + t'' D\eta'' - p' \nu v' - p'' \nu v'', \quad (83)$$

i. e., by (12),

$$\mu_1' Dm_1' + \mu_1'' Dm_1'' + \mu_2' Dm_2' + \mu_2'' Dm_2'' + \text{etc.} \leq 0, \quad (84)$$

or

$$(\mu_1'' - \mu_1') Dm_1'' + (\mu_2'' - \mu_2') Dm_2'' + \text{etc.} \leq 0. \quad (85)$$

It is evident that the sign  $=$  holds true only in the limiting case in which no motion takes place.

#### DEFINITION AND PROPERTIES OF FUNDAMENTAL EQUATIONS.

The solution of the problems of equilibrium which we have been considering has been made to depend upon the equations which express the relations between the energy, entropy, volume, and the quantities of the various components, for homogeneous combinations of the substances which are found in the given mass. The nature of such equations must be determined by experiment. As, however, it is only *differences* of energy and of entropy that can be measured, or indeed, that have a physical meaning, the values of these quantities are so far arbitrary, that we may choose independently for each simple substance the state in which its energy and its entropy are both zero. The values of the energy and the entropy of any compound body in any particular state will then be fixed. Its energy will be the sum of the work and heat expended in bringing its components from the states in which their energies and their entropies are zero into combination and to the state in question; and its entropy is the value of the integral  $\int \frac{dQ}{t}$  for any *reversible* process

by which that change is effected ( $dQ$  denoting an element of the heat communicated to the matter thus treated, and  $t$  the temperature of the matter receiving it). In the determination both of the energy and of the entropy, it is understood that at the close of the process, all bodies which have been used, other than those to which the determinations relate, have been restored to their original state, with the exception of the sources of the work and heat expended, which must be used only as such sources.

We know, however, *a priori*, that if the quantity of any homogeneous mass containing  $n$  independently variable components varies and not its nature or state, the quantities  $\varepsilon, \eta, v, m_1, m_2, \dots m_n$  will all vary in the same proportion; therefore it is sufficient if we learn from experiment the relation between all but any one of these quantities for a given constant value of that one. Or, we may consider that we have to learn from experiment the relation subsisting between the  $n + 2$  ratios of the  $n + 3$  quantities  $\varepsilon, \eta, v, m_1, m_2,$

$\dots m_n$ . To fix our ideas we may take for these ratios  $\frac{\varepsilon}{v}, \frac{\eta}{v}, \frac{m_1}{v}, \frac{m_2}{v},$

etc., that is, the separate densities of the components, and the ratios

$\frac{\varepsilon}{v}$  and  $\frac{\eta}{v}$ , which may be called the *densities of energy and entropy*.

But when there is but one component, it may be more convenient to

choose  $\frac{\varepsilon}{m}, \frac{\eta}{m}, \frac{v}{m}$  as the three variables. In any case, it is only a function of  $n + 1$  independent variables, of which the form is to be determined by experiment.

Now if  $\varepsilon$  is a known function of  $\eta, v, m_1, m_2, \dots m_n$ , as by equation (12)

$$d\varepsilon = t d\eta - p dv + \mu_1 dm_1 + \mu_2 dm_2 \dots + \mu_n dm_n, \quad (86)$$

$t, p, \mu_1, \mu_2, \dots \mu_n$  are functions of the same variables, which may be derived from the original function by differentiation, and may therefore be considered as known functions. This will make  $n + 3$  independent known relations between the  $2n + 5$  variables,  $\varepsilon, \eta, v, m_1, m_2, \dots m_n, t, p, \mu_1, \mu_2, \dots \mu_n$ . These are all that exist, for of these variables,  $n + 2$  are evidently independent. Now upon these relations depend a very large class of the properties of the compound considered,—we may say in general, all its thermal, mechanical, and chemical properties, so far as *active tendencies* are concerned, in cases in which the form of the mass does not require consideration. A single equation from which all these relations may



be deduced we will call a *fundamental equation* for the substance in question. We shall hereafter consider a more general form of the fundamental equation for solids, in which the pressure at any point is not supposed to be the same in all directions. But for masses subject only to isotropic stresses an equation between  $\varepsilon, \eta, v, m_1, m_2, \dots, m_n$  is a fundamental equation. There are other equations which possess this same property.\*

Let

$$\psi = \varepsilon - t\eta, \quad (87)$$

then by differentiation and comparison with (86) we obtain

$$d\psi = -\eta dt - p dv + \mu_1 dm_1 + \mu_2 dm_2 \dots + \mu_n dm_n. \quad (88)$$

If, then,  $\psi$  is known as a function of  $t, v, m_1, m_2, \dots, m_n$ , we can find  $\eta, p, \mu_1, \mu_2, \dots, \mu_n$  in terms of the same variables. If we then substitute for  $\psi$  in our original equation its value taken from eq. (87), we shall have again  $n+3$  independent relations between the same  $2n+5$  variables as before.

Let

$$\chi = \varepsilon + p v, \quad (89)$$

then by (86),

$$d\chi = t d\eta + v dp + \mu_1 dm_1 + \mu_2 dm_2 \dots + \mu_n dm_n. \quad (90)$$

If, then,  $\chi$  be known as a function of  $\eta, p, m_1, m_2, \dots, m_n$ , we can find  $t, v, \mu_1, \mu_2, \dots, \mu_n$  in terms of the same variables. By eliminating  $\chi$ , we may obtain again  $n+3$  independent relations between the same  $2n+5$  variables as at first.

Let

$$\zeta = \varepsilon - t\eta + p v, \quad (91)$$

then, by (86)

$$d\zeta = -\eta dt + v dp + \mu_1 dm_1 + \mu_2 dm_2 \dots + \mu_n dm_n. \quad (92)$$

If, then,  $\zeta$  is known as a function of  $t, p, m_1, m_2, \dots, m_n$ , we can

\* M. Massieu (Comptes Rendus, T. lxxix, 1869, p. 858 and p. 1057) has shown how all the properties of a fluid "which are considered in thermodynamics" may be deduced from a single function, which he calls a characteristic function of the fluid considered. In the papers cited, he introduces two different functions of this kind; viz., a function of the temperature and volume, which he denotes by  $\psi$ , the value of which in our notation would be  $\frac{-\varepsilon + t\eta}{t}$  or  $\frac{-\psi}{t}$ ; and a function of the temperature and pressure, which he denotes by  $\psi'$ , the value of which in our notation would be  $\frac{-\varepsilon + t\eta - pv}{t}$  or  $\frac{-\zeta}{t}$ . In both cases he considers a constant quantity (one kilogram) of the fluid, which is regarded as invariable in composition.

find  $\eta, v, \mu_1, \mu_2, \dots \mu_n$  in terms of the same variables. By eliminating  $\zeta$ , we may obtain again  $n + 3$  independent relations between the same  $2n + 5$  variables as at first.

If we integrate (86), supposing the quantity of the compound substance considered to vary from zero to any finite value, its nature and state remaining unchanged, we obtain

$$\varepsilon = t\eta - pv + \mu_1 m_1 + \mu_2 m_2 \dots + \mu_n m_n, \quad (93)$$

and by (87), (89), (91)

$$\psi = -pv + \mu_1 m_1 + \mu_2 m_2 \dots + \mu_n m_n, \quad (94)$$

$$\chi = t\eta + \mu_1 m_1 + \mu_2 m_2 \dots + \mu_n m_n, \quad (95)$$

$$\zeta = \mu_1 m_1 + \mu_2 m_2 \dots + \mu_n m_n. \quad (96)$$

The last three equations may also be obtained directly by integrating (88), (90), and (92).

If we differentiate (93) in the most general manner, and compare the result with (86), we obtain

$$-v dp + \eta dt + m_1 d\mu_1 + m_2 d\mu_2 \dots + m_n d\mu_n = 0, \quad (97)$$

or

$$dp = \frac{\eta}{v} dt + \frac{m_1}{v} d\mu_1 + \frac{m_2}{v} d\mu_2 \dots + \frac{m_n}{v} d\mu_n = 0. \quad (98)$$

Hence, there is a relation between the  $n + 2$  quantities  $t, p, \mu_1, \mu_2, \dots \mu_n$ , which, if known, will enable us to find in terms of these quantities all the ratios of the  $n + 2$  quantities  $\eta, v, m_1, m_2 \dots m_n$ . With (93), this will make  $n + 3$  independent relations between the same  $2n + 5$  variables as at first.

Any equation, therefore, between the quantities

$$\varepsilon, \quad \eta, \quad v, \quad m_1, \quad m_2, \dots m_n, \quad (99)$$

$$\text{or} \quad \psi, \quad t, \quad v, \quad m_1, \quad m_2, \dots m_n, \quad (100)$$

$$\text{or} \quad \chi, \quad \eta, \quad p, \quad m_1, \quad m_2, \dots m_n, \quad (101)$$

$$\text{or} \quad \zeta, \quad t, \quad p, \quad m_1, \quad m_2, \dots m_n, \quad (102)$$

$$\text{or} \quad t, \quad p, \quad \mu_1, \quad \mu_2, \dots \mu_n, \quad (103)$$

is a fundamental equation, and any such is entirely equivalent to any other.\* For any homogeneous mass whatever, considered (in general) as variable in composition, in quantity, and in thermodynamic state, and having  $n$  independently variable components, to which

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\* The distinction between equations which are, and which are not, *fundamental*, in the sense in which the word is here used, may be illustrated by comparing an equation

the subscript numerals refer, (but not excluding the case in which  $n = 1$  and the composition of the body is invariable,) there is a relation between the quantities enumerated in any one of the above sets, from which, if known, with the aid only of *general* principles and relations, we may deduce all the relations subsisting for such a mass between the quantities  $\varepsilon, \psi, \chi, \zeta, \eta, v, m_1, m_2, \dots m_n, t, p, \mu_1, \mu_2, \dots \mu_n$ . It will be observed that, besides the equations which define  $\psi, \chi$ , and  $\zeta$ , there is one finite equation, (93), which subsists between these quantities independently of the form of the fundamental equation.

Other sets of quantities might of course be added which possess the same property. The sets (100), (101), (102) are mentioned on account of the important properties of the quantities  $\psi, \chi, \zeta$ , and because the equations (88), (90), (92), like (86), afford convenient definitions of the potentials, viz.,

$$\mu_1 = \left( \frac{d\varepsilon}{dm_1} \right)_{\eta, v, m} = \left( \frac{d\psi}{dm_1} \right)_{t, v, m} = \left( \frac{d\chi}{dm_1} \right)_{\eta, p, m} = \left( \frac{d\zeta}{dm_1} \right)_{t, p, m} \quad (104)$$

etc., where the subscript letters denote the quantities which remain constant in the differentiation,  $m$  being written for brevity for all the letters  $m_1, m_2, \dots m_n$  except the one occurring in the denominator. It will be observed that the quantities in (103) are all independent of the quantity of the mass considered, and are those which must, in general, have the same value in contiguous masses in equilibrium.

*On the quantities  $\psi, \chi, \zeta$ .*

The quantity  $\psi$  has been defined for any homogeneous mass by the equation

$$\psi = \varepsilon - t\eta. \quad (105)$$

between

$$\varepsilon, \eta, v, m_1, m_2, \dots m_n$$

with one between

$$\varepsilon, t, v, m_1, m_2, \dots m_n.$$

As, by (86),

$$t = \left( \frac{d\varepsilon}{d\eta} \right)_{v, m},$$

the second equation may evidently be derived from the first. But the first equation cannot be derived from the second; for an equation between

$$\varepsilon, \left( \frac{d\varepsilon}{d\eta} \right)_{v, m}, v, m_1, m_2, \dots m_n$$

is equivalent to one between

$$\left( \frac{d\eta}{d\varepsilon} \right)_{v, m}, \varepsilon, v, m_1, m_2, \dots m_n.$$

which is evidently not sufficient to determine the value of  $\eta$  in terms of the other variables.



We may extend this definition to any material system whatever which has a uniform temperature throughout.

If we compare two states of the system of the same temperature, we have

$$\psi' - \psi'' = \varepsilon' - \varepsilon'' - t(\eta' - \eta''). \quad (106)$$

If we suppose the system brought from the first to the second of these states without change of temperature and by a reversible process in which  $W$  is the work done and  $Q$  the heat received by the system, then

$$\varepsilon' - \varepsilon'' = W - Q, \quad (107)$$

$$\text{and} \quad t(\eta'' - \eta') = Q. \quad (108)$$

Hence

$$\psi' - \psi'' = W; \quad (109)$$

and for an infinitely small reversible change in the state of the system, in which the temperature remains constant, we may write

$$-d\psi = dW. \quad (110)$$

Therefore,  $-\psi$  is the force function of the system for constant temperature, just as  $-\varepsilon$  is the force function for constant entropy. That is, if we consider  $\psi$  as a function of the temperature and the variables which express the distribution of the matter in space, for every different value of the temperature  $-\psi$  is the different force function required by the system if maintained at that special temperature.

From this we may conclude that when a system has a uniform temperature throughout, the additional conditions which are necessary and sufficient for equilibrium may be expressed by

$$(\delta\psi)_t \geq 0. * \quad (111)$$

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\* This general condition of equilibrium might be used instead of (2) in such problems of equilibrium as we have considered and others which we shall consider hereafter with evident advantage in respect to the brevity of the formulæ, as the limitation expressed by the subscript  $t$  in (111) applies to every part of the system taken separately, and diminishes by one the number of independent variations in the state of these parts which we have to consider. The more cumbersome course adopted in this paper has been chosen, among other reasons, for the sake of deducing *all* the particular conditions of equilibrium from one general condition, and of having the quantities mentioned in this general condition such as are most generally used and most simply defined; and because in the longer formulæ as given, the reader will easily see in each case the form which they would take if we should adopt (111) as the general condition of equilibrium, which would be in effect to take the thermal condition of equilibrium for granted, and to seek only the remaining conditions. For example, in the problem treated on pages 116 ff., we would obtain from (111) by (88) a condition precisely like (15), except that the terms  $t\delta\eta'$ ,  $t\delta\eta''$ , etc. would be wanting.

When it is not possible to bring the system from one to the other of the states to which  $\psi'$  and  $\psi''$  relate by a reversible process without altering the temperature, it will be observed that it is not necessary for the validity of (107)–(109) that the temperature of the system should remain constant during the reversible process to which  $W$  and  $Q$  relate, provided that the only source of heat or cold used has the same temperature as the system in its initial or final state. Any external bodies may be used in the process in any way not affecting the condition of reversibility, if restored to their original condition at the close of the process; nor does the limitation in regard to the use of heat apply to such heat as may be restored to the source from which it has been taken.

It may be interesting to show directly the equivalence of the conditions (111) and (2) when applied to a system of which the temperature in the given state is uniform throughout.

If there are any variations in the state of such a system which do not satisfy (2), then for these variations

$$\delta\varepsilon < 0 \quad \text{and} \quad \delta\eta = 0.$$

If the temperature of the system in its varied state is not uniform, we may evidently increase its entropy without altering its energy by supposing heat to pass from the warmer to the cooler parts. And the state having the greatest entropy for the energy  $\varepsilon + \delta\varepsilon$  will necessarily be a state of uniform temperature. For this state (regarded as a variation from the original state)

$$\delta\varepsilon < 0 \quad \text{and} \quad \delta\eta > 0.$$

Hence, as we may diminish both the energy and the entropy by cooling the system, there must be a state of uniform temperature for which (regarded as a variation of the original state)

$$\delta\varepsilon < 0 \quad \text{and} \quad \delta\eta = 0.$$

From this we may conclude that for systems of initially uniform temperature condition (2) will not be altered if we limit the variations to such as do not disturb the uniformity of temperature.

Confining our attention, then, to states of uniform temperature, we have by differentiation of (105)

$$\delta\varepsilon - t\delta\eta = \delta\psi + \eta\delta t. \quad (112)$$

Now there are evidently changes in the system (produced by heating or cooling) for which

$$\delta\varepsilon - t\delta\eta = 0 \quad \text{and therefore} \quad \delta\psi + \eta\delta t = 0, \quad (113)$$

neither  $\delta\eta$  nor  $\delta t$  having the value zero. This consideration is sufficient to show that the condition (2) is equivalent to

$$\delta\varepsilon - t\delta\eta \geq 0. \quad (114)$$

and that the condition (111) is equivalent to

$$\delta\psi + \eta\delta t \geq 0 \quad (115)$$

and by (112) the two last conditions are equivalent.

In such cases as we have considered on pages 115–137, in which the form and position of the masses of which the system is composed is immaterial, uniformity of temperature and pressure are always necessary for equilibrium, and the remaining conditions, when these are satisfied, may be conveniently expressed by means of the function  $\zeta$ , which has been defined for a homogeneous mass on page 142, and which we will here define for any mass of uniform temperature and pressure by the same equation

$$\zeta = \varepsilon - t\eta + pv. \quad (116)$$

For such a mass, the condition of (internal) equilibrium is

$$(\delta\zeta)_{t,p} \geq 0. \quad (117)$$

That this condition is equivalent to (2) will easily appear from considerations like those used in respect to (111).

Hence, it is necessary for the equilibrium of two contiguous masses identical in composition that the values of  $\zeta$  as determined for equal quantities of the two masses should be equal. Or, when one of three contiguous masses can be formed out of the other two, it is necessary for equilibrium that the value of  $\zeta$  for any quantity of the first mass should be equal to the sum of the values of  $\zeta$  for such quantities of the second and third masses as together contain the same matter. Thus, for the equilibrium of a solution composed of  $a$  parts of water and  $b$  parts of a salt which is in contact with vapor of water and crystals of the salt, it is necessary that the value of  $\zeta$  for the quantity  $a+b$  of the solution should be equal to the sum of the values of  $\zeta$  for the quantities  $a$  of the vapor and  $b$  of the salt. Similar propositions will hold true in more complicated cases. The reader will easily deduce these conditions from the particular conditions of equilibrium given on page 128.

In like manner we may extend the definition of  $\chi$  to any mass or combination of masses in which the pressure is everywhere the same, using  $\varepsilon$  for the energy and  $v$  for the volume of the whole and setting as before

$$\chi = \varepsilon + pv. \quad (118)$$

If we denote by  $Q$  the heat received by the combined masses from external sources in any process in which the pressure is not varied, and distinguish the initial and final states of the system by accents we have

$$\chi'' - \chi' = \varepsilon'' - \varepsilon' + p(v'' - v') = Q. \quad (119)$$

This function may therefore be called the *heat function for constant pressure* (just as the energy might be called the heat function for constant volume), the diminution of the function representing in all cases in which the pressure is not varied the heat given out by the system. In all cases of chemical action in which no heat is allowed to escape the value of  $\chi$  remains unchanged.

#### POTENTIALS.

In the definition of the potentials  $\mu_1, \mu_2$ , etc., the energy of a homogeneous mass was considered as a function of its entropy, its volume, and the quantities of the various substances composing it. Then the potential for one of these substances was defined as the differential coefficient of the energy taken with respect to the variable expressing the quantity of that substance. Now, as the manner in which we consider the given mass as composed of various substances is in some degree arbitrary, so that the energy may be considered as a function of various different sets of variables expressing quantities of component substances, it might seem that the above definition does not fix the value of the potential of any substance in the given mass, until we have fixed the manner in which the mass is to be considered as composed. For example, if we have a solution obtained by dissolving in water a certain salt containing water of crystallization, we may consider the liquid as composed of  $m_s$  weight-units of the hydrate and  $m_w$  of water, or as composed of  $m_s$  of the anhydrous salt and  $m_w$  of water. It will be observed that the values of  $m_s$  and  $m_w$  are not the same, nor those of  $m_w$  and  $m_w$ , and hence it might seem that the potential for water in the given liquid considered as composed of the hydrate and water, viz.,

$$\left( \frac{d\varepsilon}{dm_w} \right)_{\eta, v, m_s}$$

would be different from the potential for water in the same liquid considered as composed of anhydrous salt and water, viz.,

$$\left( \frac{d\varepsilon}{dm_w} \right)_{\eta, v, m_s}$$



The value of the two expressions is, however, the same, for, although  $m_w$  is not equal to  $m_w$ , we may of course suppose  $dm_w$  to be equal to  $dm_w$ , and then the numerators in the two fractions will also be equal, as they each denote the increase of energy of the liquid, when the quantity  $dm_w$  or  $dm_w$  of water is added without altering the entropy and volume of the liquid. Precisely the same considerations will apply to any other case.

In fact, we may give a definition of a potential which shall not presuppose any choice of a particular set of substances as the components of the homogeneous mass considered.

*Definition.*—If to any homogeneous mass we suppose an infinitesimal quantity of any substance to be added, the mass remaining homogeneous and its entropy and volume remaining unchanged, the increase of the energy of the mass divided by the quantity of the substance added is the *potential* for that substance in the mass considered. (For the purposes of this definition, any chemical element or combination of elements in given proportions may be considered a substance, whether capable or not of existing by itself as a homogeneous body.)

In the above definition we may evidently substitute for entropy, volume, and energy, respectively, either temperature, volume, and the function  $\psi$ ; or entropy, pressure, and the function  $\chi$ ; or temperature, pressure, and the function  $\xi$ . (Compare equation (104).)

In the same homogeneous mass, therefore, we may distinguish the potentials for an indefinite number of substances, each of which has a perfectly determined value.

Between the potentials for different substances in the same homogeneous mass the same equations will subsist as between the units of these substances. That is, if the substances,  $S_a, S_b$ , etc.,  $S_k, S_l$ , etc., are components of any given homogeneous mass, and are such that

$$\alpha \mathcal{E}_a + \beta \mathcal{E}_b + \text{etc.} = \kappa \mathcal{E}_k + \lambda \mathcal{E}_l + \text{etc.}, \quad (120)$$

$\mathcal{E}_a, \mathcal{E}_b$ , etc.,  $\mathcal{E}_k, \mathcal{E}_l$ , etc. denoting the units of the several substances, and  $\alpha, \beta$ , etc.,  $\kappa, \lambda$ , etc. denoting numbers, then if  $\mu_a, \mu_b$ , etc.,  $\mu_k, \mu_l$ , etc. denote the potentials for these substances in the homogeneous mass,

$$\alpha \mu_a + \beta \mu_b + \text{etc.} = \kappa \mu_k + \lambda \mu_l + \text{etc.} \quad (121)$$

To show this, we will suppose the mass considered to be very large. Then, the first number of (121) denotes the increase of the energy of the mass produced by the addition of the matter represented by the first member of (120), and the second member of (121) denotes the

increase of energy of the same mass produced by the addition of the matter represented by the second member of (120), the entropy and volume of the mass remaining in each case unchanged. Therefore, as the two members of (120) represent the same matter in kind and quantity, the two members of (121) must be equal.

But it must be understood that equation (120) is intended to denote equivalence of the substances represented *in the mass considered*, and not merely chemical identity; in other words, it is supposed that there are no passive resistances to change in the mass considered which prevent the substances represented by one member of (120) from passing into those represented by the other. For example, in respect to a mixture of vapor of water and free hydrogen and oxygen (at ordinary temperatures), we may not write

$$9 \mathfrak{S}_{Aq} = 1 \mathfrak{S}_H + 8 \mathfrak{S}_O,$$

but water is to be treated as an independent substance, and no necessary relation will subsist between the potential for water and the potentials for hydrogen and oxygen.

The reader will observe that the relations expressed by equations (43) and (51) (which are essentially relations between the potentials for actual components in different parts of a mass in a state of equilibrium) are simply those which by (121) would necessarily subsist between the same potentials in any homogeneous mass containing as variable components all the substances to which the potentials relate.

In the case of a body of invariable composition, the potential for the single component is equal to the value of  $\zeta$  for one unit of the body, as appears from the equation

$$\zeta = \mu m \tag{122}$$

to which (96) reduces in this case. Therefore, when  $n = 1$ , the fundamental equation between the quantities in the set (102) (see page 143) and that between the quantities in (103) may be derived either from the other by simple substitution. But, with this single exception, an equation between the quantities in one of the sets (99)–(103) cannot be derived from the equation between the quantities in another of these sets without differentiation.

Also in the case of a body of variable composition, when all the quantities of the components except one vanish, the potential for that one will be equal to the value of  $\zeta$  for one unit of the body. We may make this occur for any given composition of the body by

choosing as one of the components the matter constituting the body itself, so that the value of  $\zeta$  for one unit of a body may always be considered as a potential. Hence the relations between the values of  $\zeta$  for contiguous masses given on page 147 may be regarded as relations between potentials.

The two following propositions afford definitions of a potential which may sometimes be convenient.

The potential for any substance in any homogeneous mass is equal to the amount of mechanical work required to bring a unit of the substance by a reversible process from the state in which its energy and entropy are both zero into combination with the homogeneous mass, which at the close of the process must have its original volume, and which is supposed so large as not to be sensibly altered in any part. All other bodies used in the process must by its close be restored to their original state, except those used to supply the work, which must be used only as the source of the work. For, in a reversible process, when the entropies of other bodies are not altered, the entropy of the substance and mass taken together will not be altered. But the original entropy of the substance is zero; therefore the entropy of the mass is not altered by the addition of the substance. Again, the work expended will be equal to the increment of the energy of the mass and substance taken together, and therefore equal, as the original energy of the substance is zero, to the increment of energy of the mass due to the addition of the substance, which by the definition on page 149 is equal to the potential in question.

' The potential for any substance in any homogeneous mass is equal to the work required to bring a unit of the substance by a reversible process from a state in which  $\psi = 0$  and the temperature is the same as that of the given mass into combination with this mass, which at the close of the process must have the same volume and temperature as at first, and which is supposed so large as not to be sensibly altered in any part. A source of heat or cold of the temperature of the given mass is allowed, with this exception, other bodies are to be used only on the same conditions as before. This may be shown by applying equation (109) to the mass and substance taken together.

The last proposition enables us to see very easily, how the value of the potential is affected by the arbitrary constants involved in the definition of the energy and the entropy of each elementary substance. For we may imagine the substance brought from the state in which  $\psi = 0$  and the temperature is the same as that of the given

mass, first to any specified state of the same temperature, and then into combination with the given mass. In the first part of the process the work expended is evidently represented by the value of  $\psi$  for the unit of the substance in the state specified. Let this be denoted by  $\psi'$ , and let  $\mu$  denote the potential in question, and  $W$  the work expended in bringing a unit of the substance from the specified state into combination with the given mass as aforesaid; then

$$\mu = \psi' + W. \quad (123)$$

Now as the state of the substance for which  $\varepsilon = 0$  and  $\eta = 0$  is arbitrary, we may simultaneously increase the energies of the unit of the substance in all possible states by any constant  $C$ , and the entropies of the substance in all possible states by any constant  $K$ . The value of  $\psi$ , or  $\varepsilon - t\eta$ , for any state would then be increased by  $C - tK$ ,  $t$  denoting the temperature of the state. Applying this to  $\psi'$  in (123) and observing that the last term in this equation is independent of the values of these constants, we see that the potential would be increased by the same quantity  $C - tK$ ,  $t$  being the temperature of the mass in which the potential is to be determined.

#### ON COEXISTENT PHASES OF MATTER.

In considering the different homogeneous bodies which can be formed out of any set of component substances, it will be convenient to have a term which shall refer solely to the composition and thermodynamic state of any such body without regard to its quantity or form. We may call such bodies as differ in composition or state different *phases* of the matter considered, regarding all bodies which differ only in quantity and form as different examples of the same phase. Phases which can exist together, the dividing surfaces being plane, in an equilibrium which does not depend upon passive resistances to change, we shall call *coexistent*.

If a homogeneous body has  $n$  independently variable components, the phase of the body is evidently capable of  $n + 1$  independent variations. A system of  $r$  coexistent phases, each of which has the same  $n$  independently variable components is capable of  $n + 2 - r$  variations of phase. For the temperature, the pressure, and the potentials for the actual components have the same values in the different phases, and the variations of these quantities are by (97) subject to as many conditions as there are different phases. Therefore, the number of independent variations in the values of these quantities, i. e., the number of independent variations of phase of the system, will be  $n + 2 - r$ .



Or, when the  $r$  bodies considered have not the same independently variable components, if we still denote by  $n$  the number of independently variable components of the  $r$  bodies taken as a whole, the number of independent variations of phase of which the system is capable will still be  $n+2-r$ . In this case, it will be necessary to consider the potentials for more than  $n$  component substances. Let the number of these potentials be  $n+h$ . We shall have by (97), as before,  $r$  relations between the variations of the temperature, of the pressure, and of these  $n+h$  potentials, and we shall also have by (43) and (51)  $h$  relations between these potentials, of the same form as the relations which subsist between the units of the different component substances.

Hence, if  $r = n + 2$ , no variation in the phases (remaining coexistent) is possible. It does not seem probable that  $r$  can ever exceed  $n + 2$ . An example of  $n = 1$  and  $r = 3$  is seen in the coexistent solid, liquid, and gaseous forms of any substance of invariable composition. It seems not improbable that in the case of sulphur and some other simple substances there is more than one triad of coexistent phases; but it is entirely improbable that there are four coexistent phases of any simple substance. An example of  $n = 2$  and  $r = 4$  is seen in a solution of a salt in water in contact with vapor of water and two different kinds of crystals of the salt.

#### *Concerning $n + 1$ Coexistent Phases.*

We will now seek the differential equation which expresses the relation between the variations of the temperature and the pressure in a system of  $n + 1$  coexistent phases ( $n$  denoting, as before, the number of independently variable components in the system taken as a whole).

In this case we have  $n + 1$  equations of the general form of (97) (one for each of the coexistent phases), in which we may distinguish the quantities  $\eta$ ,  $v$ ,  $m_1$ ,  $m_2$ , etc. relating to the different phases by accents. But  $t$  and  $p$  will each have the same value throughout, and the same is true of  $\mu_1$ ,  $\mu_2$ , etc., so far as each of these occurs in the different equations. If the total number of these potentials is  $n + h$ , there will be  $h$  independent relations between them, corresponding to the  $h$  independent relations between the units of the component substances to which the potentials relate, by means of which we may eliminate the variations of  $h$  of the potentials from the equations of the form of (97) in which they occur.

Let one of these equations be

$$v' dp = \eta' dt + m_a' d\mu_a + m_b' d\mu_b + \text{etc.}, \quad (124)$$

and by the proposed elimination let it become

$$v' dp = \eta' dt + A_1' d\mu_1 + A_2' d\mu_2 \dots + A_n' d\mu_n. \quad (125)$$

It will be observed that  $\mu_a$ , for example, in (124) denotes the potential in the mass considered for a substance  $S_a$  which may or may not be identical with any of the substances  $S_1, S_2$ , etc. to which the potentials in (125) relate. Now as the equations between the potentials by means of which the elimination is performed are similar to those which subsist between the units of the corresponding substances, (compare equations (38), (43), and (51)), if we denote these units by  $\mathfrak{S}_a, \mathfrak{S}_b$ , etc.,  $\mathfrak{S}_1, \mathfrak{S}_2$ , etc., we must also have

$$m_a' \mathfrak{S}_a + m_b' \mathfrak{S}_b + \text{etc.} = A_1' \mathfrak{S}_1 + A_2' \mathfrak{S}_2 \dots + A_n' \mathfrak{S}_n. \quad (126)$$

But the first member of this equation denotes (in kind and quantity) the matter in the body to which equations (124) and (125) relate. As the same must be true of the second member, we may regard this same body as composed of the quantity  $A_1'$  of the substance  $S_1$ , with the quantity  $A_2'$  of the substance  $S_2$ , etc. We will therefore, in accordance with our general usage, write  $m_1', m_2'$ , etc. for  $A_1', A_2'$ , etc. in (125), which will then become

$$v' dp = \eta' dt + m_1' d\mu_1 + m_2' d\mu_2 \dots + m_n' d\mu_n. \quad (127)$$

But we must remember that the components to which the  $m_1', m_2'$ , etc. of this equation relate are not necessarily independently variable, as are the components to which the similar expressions in (97) and (124) relate. The rest of the  $n + 1$  equations may be reduced to a similar form, viz.,

$$v'' dp = \eta'' dt + m_1'' d\mu_1 + m_2'' d\mu_2 \dots + m_n'' d\mu_n, \quad (128)$$

etc.

By elimination of  $d\mu_1, d\mu_2, \dots, d\mu_n$  from these equations we obtain

$$\begin{vmatrix} v' & m_1' & m_2' & \dots & m_n' \\ v'' & m_1'' & m_2'' & \dots & m_n'' \\ v''' & m_1''' & m_2''' & \dots & m_n''' \\ \cdot & \cdot & \cdot & \dots & \cdot \\ \cdot & \cdot & \cdot & \dots & \cdot \end{vmatrix} dp = \begin{vmatrix} \eta' & m_1' & m_2' & \dots & m_n' \\ \eta'' & m_1'' & m_2'' & \dots & m_n'' \\ \eta''' & m_1''' & m_2''' & \dots & m_n''' \\ \cdot & \cdot & \cdot & \dots & \cdot \\ \cdot & \cdot & \cdot & \dots & \cdot \end{vmatrix} dt. \quad (129)$$

In this equation we may make  $v', v''$ , etc. equal to unity. Then  $m_1', m_2', m_1''$ , etc. will denote the separate densities of the components in the different phases, and  $\eta', \eta''$ , etc. the densities of entropy.

When  $n = 1$ ,

$$(m'' v' - m' v'') dp = (m'' \eta' - m' \eta'') dt, \quad (130)$$

or, if we make  $m' = 1$  and  $m'' = 1$ , we have the usual formula

$$\frac{dp}{dt} = \frac{\eta' - \eta''}{v' - v''} = \frac{Q}{t(v'' - v')}, \quad (131)$$

in which  $Q$  denotes the heat absorbed by a unit of the substance in passing from one state to the other without change of temperature or pressure.

*Concerning Cases in which the Number of Coexistent Phases is less than  $n + 1$ .*

When  $n > 1$ , if the quantities of all the components  $S_1, S_2, \dots S_n$  are proportional in two coexistent phases, the two equations of the form of (127) and (128) relating to these phases will be sufficient for the elimination of the variations of all the potentials. In fact, the condition of the coexistence of the two phases together with the condition of the equality of the  $n - 1$  ratios of  $m_1', m_2', \dots m_n'$  with the  $n - 1$  ratios of  $m_1'', m_2'', \dots m_n''$  is sufficient to determine  $p$  as a function of  $t$  if the fundamental equation is known for each of the phases. The differential equation in this case may be expressed in the form of (130),  $m'$  and  $m''$  denoting either the quantities of any one of the components or the total quantities of matter in the bodies to which they relate. Equation (131) will also hold true in this case, if the total quantity of matter in each of the bodies is unity. But this case differs from the preceding in that the matter which absorbs the heat  $Q$  in passing from one state to another, and to which the other letters in the formula relate, although the same in quantity, is not in general the same in kind at different temperatures and pressures. Yet the case will often occur that one of the phases is essentially invariable in composition, especially when it is a crystalline body, and in this case the matter to which the letters in (131) relate will not vary with the temperature and pressure.

When  $n = 2$ , two coexistent phases are capable, when the temperature is constant, of a single variation in phase. But as (130) will hold true in this case when  $m_1' : m_2' :: m_1'' : m_2''$ , it follows that for constant temperature the pressure is in general a maximum or a minimum when the composition of the two phases is identical. In like manner, the temperature of the two coexistent phases is in general a maximum or a minimum, for constant pressure, when the composition of the two phases is identical. Hence, the series of simultaneous values of  $t$  and  $p$  for which the composition of two coexistent phases

is identical separates those simultaneous values of  $t$  and  $p$  for which no coexistent phases are possible from those for which there are two pair of coexistent phases. This may be applied to a liquid having two independently variable components in connection with the vapor which it yields, or in connection with any solid which may be formed in it.

When  $n = 3$ , we have for three coexistent phases three equations of the form of (127), from which we may obtain the following,

$$\begin{vmatrix} v' & m_1' & m_2' \\ v'' & m_1'' & m_2'' \\ v''' & m_1''' & m_2''' \end{vmatrix} dp = \begin{vmatrix} \eta' & m_1' & m_2' \\ \eta'' & m_1'' & m_2'' \\ \eta''' & m_1''' & m_2''' \end{vmatrix} dt + \begin{vmatrix} m_1' & m_2' & m_3' \\ m_1'' & m_2'' & m_3'' \\ m_1''' & m_2''' & m_3''' \end{vmatrix} d\mu_3. \quad (132)$$

Now the value of the last of these determinants will be zero, when the composition of one of the three phases is such as can be produced by combining the other two. Hence, the pressure of three coexistent phases will in general be a maximum or minimum for constant temperature, and the temperature a maximum or minimum for constant pressure, when the above condition in regard to the composition of the coexistent phases is satisfied. The series of simultaneous values of  $t$  and  $p$  for which the condition is satisfied separates those simultaneous values of  $t$  and  $p$  for which three coexistent phases are not possible, from those for which there are two triads of coexistent phases. These propositions may be extended to higher values of  $n$ , and illustrated by the boiling temperatures and pressures of saturated solutions of  $n - 2$  different solids in solvents having two independently variable components.

#### INTERNAL STABILITY OF HOMOGENEOUS FLUIDS AS INDICATED BY FUNDAMENTAL EQUATIONS.

We will now consider the stability of a fluid enclosed in a rigid envelop which is non-conducting to heat and impermeable to all the components of the fluid. The fluid is supposed initially homogeneous in the sense in which we have before used the word, i. e., uniform in every respect throughout its whole extent. Let  $S_1, S_2, \dots S_n$  be the *ultimate* components of the fluid; we may then consider every body which can be formed out of the fluid to be composed of  $S_1, S_2, \dots S_n$ , and that in only one way. Let  $m_1, m_2, \dots m_n$  denote the quantities of these substances in any such body, and let  $\varepsilon, \eta, v$ , denote its energy, entropy, and volume. The fundamental equation for compounds of  $S_1, S_2, \dots S_n$ , if completely determined, will give us all possible sets of simultaneous values of these variables for homogeneous bodies.



Now, if it is possible to assign such values to the constants  $T$ ,  $P$ ,  $M_1$ ,  $M_2$ , . . .  $M_n$  that the value of the expression

$$\varepsilon - T\eta + Pv - M_1 m_1 - M_2 m_2 \dots - M_n m_n \quad (133)$$

shall be zero for the given fluid, and shall be positive for every other phase of the same components, i. e., for every homogeneous body\* not identical in nature and state with the given fluid (but composed entirely of  $S_1$ ,  $S_2$ , . . .  $S_n$ ), the condition of the given fluid will be stable.

For, in any condition whatever of the given mass, whether or not homogeneous, or fluid, if the value of the expression (133) is not negative for any homogeneous part of the mass, its value for the whole mass cannot be negative; and if its value cannot be zero for any homogeneous part which is not identical in phase with the mass in its given condition, its value cannot be zero for the whole except when the whole is in the given condition. Therefore, in the case supposed, the value of this expression for any other than the given condition of the mass is positive. (That this conclusion cannot be invalidated by the fact that it is not entirely correct to regard a composite mass as made up of homogeneous parts having the same properties in respect to energy, entropy, etc., as if they were parts of larger homogeneous masses, will easily appear from considerations similar to those adduced on pages 131-133.) If, then, the value of the expression (133) for the mass considered is less when it is in the given condition than when it is in any other, the energy of the mass in its given condition must be less than in any other condition in which it has the same entropy and volume. The given condition is therefore stable. (See page 110.)

Again, if it is possible to assign such values to the constants in (133) that the value of the expression shall be zero for the given fluid mass, and shall not be negative for any phase of the same components, the given condition will be evidently not unstable. (See page 110.) It will be stable unless it is possible for the given matter in the given volume and with the given entropy to consist of homogeneous parts for all of which the value of the expression (133) is zero, but which are not all identical in phase with the mass in its given condition. (A mass consisting of such parts would be in equilibrium, as we have already seen on pages 133, 134.) In this case, if we disregard the quantities connected with the surfaces which divide the

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\* A vacuum is throughout this discussion to be regarded as a limiting case of an extremely rarified body. We may thus avoid the necessity of the specific mention of a vacuum in propositions of this kind.

homogeneous parts, we must regard the given condition as one of neutral equilibrium. But in regard to these homogeneous parts, which we may evidently consider to be all different phases, the following conditions must be satisfied. (The accents distinguish the letters referring to the different parts, and the unaccented letters refer to the whole mass.)

$$\left. \begin{aligned} \eta' + \eta'' + \text{etc.} &= \eta, \\ v' + v'' + \text{etc.} &= v, \\ m_1' + m_1'' + \text{etc.} &= m_1, \\ m_2' + m_2'' + \text{etc.} &= m_2, \\ \text{etc.} \end{aligned} \right\} \quad (134)$$

Now the values of  $\eta$ ,  $v$ ,  $m_1$ ,  $m_2$ , etc. are determined by the whole fluid mass in its given state, and the values of  $\frac{\eta'}{v}$ ,  $\frac{\eta''}{v''}$ , etc.,  $\frac{m_1'}{v'}$ ,  $\frac{m_1''}{v''}$ , etc.,  $\frac{m_2'}{v'}$ ,  $\frac{m_2''}{v''}$ , etc., etc., are determined by the phases of the various parts. But the phases of these parts are evidently determined by the phase of the fluid as given. They form, in fact, the whole set of coexistent phases of which the latter is one. Hence, we may regard (134) as  $n + 2$  linear equations between  $v'$ ,  $v''$ , etc. (The values of  $v'$ ,  $v''$ , etc. are also subject to the condition that none of them can be negative.) Now one solution of these equations must give us the given condition of the fluid; and it is not to be expected that they will be capable of any other solution, unless the number of different homogeneous parts, that is, the number of different coexistent phases, is greater than  $n + 2$ . We have already seen (page 153) that it is not probable that this is ever the case.

We may, however, remark that in a certain sense an infinitely large fluid mass will be in neutral equilibrium in regard to the formation of the substances, if such there are, other than the given fluid, for which the value of (133) is zero (when the constants are so determined that the value of the expression is zero for the given fluid, and not negative for any substance); for the tendency of such a formation to be reabsorbed will diminish indefinitely as the mass out of which it is formed increases.

When the substances  $S_1$ ,  $S_2$ , . . .  $S_n$  are all independently variable components of the given mass, it is evident from (86) that the conditions that the value of (133) shall be zero for the mass as given, and shall not be negative for any phase of the same components, can only be fulfilled when the constants  $T$ ,  $P$ ,  $M_1$ ,  $M_2$ , . . .  $M_n$  are equal to the temperature, the pressure, and the several potentials in the given

mass. If we give these values to the constants, the expression (133) will necessarily have the value zero for the given mass and we shall only have to inquire whether its value is positive for all other phases. But when  $S_1, S_2, \dots S_n$  are not all independently variable components of the given mass, the values which it will be necessary to give to the constants in (133) cannot be determined entirely from the properties of the given mass; but  $T$  and  $P$  must be equal to its temperature and pressure, and it will be easy to obtain as many equations connecting  $M_1, M_2, \dots M_n$  with the potentials in the given mass as it contains independently variable components.

When it is not possible to assign such values to the constants in (133) that the value of the expression shall be zero for the given fluid, and either zero or positive for any phase of the same components, we have already seen (pages 129–134) that if equilibrium subsists without passive resistances to change, it must be in virtue of properties which are peculiar to small masses surrounded by masses of different nature, and which are not indicated by fundamental equations. In this case, the fluid will necessarily be unstable, if we extend this term to embrace all cases in which an initial disturbance confined to a small part of an indefinitely large fluid mass will cause an ultimate change of state not indefinitely small in degree throughout the whole mass. In the discussion of stability as indicated by fundamental equations it will be convenient to use the term in this sense.\*

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\* If we wish to know the stability of the given fluid when exposed to a constant temperature, or to a constant pressure, or to both, we have only to suppose that there is enclosed in the same envelop with the given fluid another body (which cannot combine with the fluid) of which the fundamental equation is  $\epsilon = T\eta$ , or  $\epsilon = -Pv$ , or  $\epsilon = T\eta - Pv$ , as the case may be, ( $T$  and  $P$  denoting the constant temperature and pressure, which of course must be those of the given fluid,) and to apply the criteria of page 110 to the whole system. When it is possible to assign such values to the constants in (133) that the value of the expression shall be zero for the given fluid and positive for every other phase of the same components, the value of (133) for the whole system will be less when the system is in its given condition than when it is in any other. (Changes of form and position of the given fluid are of course regarded as immaterial.) Hence the fluid is stable. When it is not possible to assign such values to the constants that the value of (133) shall be zero for the given fluid and zero or positive for any other phase, the fluid is of course unstable. In the remaining case, when it is possible to assign such values to the constants that the value of (133) shall be zero for the given fluid and zero or positive for every other phase, but not without the value zero for some other phase, the state of equilibrium of the fluid as stable or neutral will be determined by the possibility of satisfying, for any other than the given condition of the fluid, equations like (134), in which, however, the first or the second or both are to be stricken out, according as we are considering the

In determining for any given positive values of  $T$  and  $P$  and any given values whatever of  $M_1, M_2, \dots M_n$  whether the expression (133) is capable of a negative value for any phase of the components  $S_1, S_2, \dots S_n$ , and if not, whether it is capable of the value zero for any other phase than that of which the stability is in question, it is only necessary to consider phases having the temperature  $T$  and pressure  $P$ . For we may assume that a mass of matter represented by any values of  $m_1, m_2, \dots m_n$  is capable of at least one state of not unstable equilibrium (which may or may not be a homogeneous state) at this temperature and pressure. It may easily be shown that for such a state the value of  $\varepsilon - T\eta + Pv$  must be as small as for any other state of the same matter. The same will therefore be true of the value of (133). Therefore if this expression is capable of a negative value for any mass whatever, it will have a negative value for that mass at the temperature  $T$  and pressure  $P$ . And if this mass is not homogeneous, the value of (133) must be negative for at least one of its homogeneous parts. So also, if the expression (133) is not capable of a negative value for any phase of the components, any phase for which it has the value zero must have the temperature  $T$  and the pressure  $P$ .

It may easily be shown that the same must be true in the limiting cases in which  $T=0$  and  $P=0$ . For negative values of  $P$ , (133) is always capable of negative values, as its value for a vacuum is  $Pv$ .

For any body of the temperature  $T$  and pressure  $P$ , the expression (133) may by (91) be reduced to the form

$$\zeta - M_1 m_1 - M_2 m_2 \dots - M_n m_n. \quad (135)$$

We have already seen (pages 131, 132) that an expression like (133), when  $T, P, M_1, M_2, \dots M_n$  and  $v$  have any given finite values, cannot have an infinite negative value as applied to any real body. Hence, in determining whether (133) is capable of a negative value for any phase of the components  $S_1, S_2, \dots S_n$ , and if not, whether it is capable of the value zero for any other phase than that of which the stability is in question, we have only to consider the least value of which it is capable for a constant value of  $v$ . Any body giving this value must satisfy the condition that for constant volume

$$d\varepsilon - T d\eta - M_1 dm_1 - M_2 dm_2 \dots - M_n dm_n \geq 0, \quad (136)$$

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stability of the fluid for constant temperature, or for constant pressure, or for both. The number of coexistent phases will sometimes exceed by one or two the number of the remaining equations, and then the equilibrium of the fluid will be neutral in respect to one or two independent changes.



or, if we substitute the value of  $d\varepsilon$  taken from equation (86), using subscript  $a \dots g$  for the quantities relating to the actual components of the body, and subscript  $h \dots k$  for those relating to the possible,

$$t d\eta + \mu_a dm_a \dots + \mu_g dm_g + \mu_h dm_h \dots + \mu_k dm_k - T d\eta - M_1 dm_1 - M_2 dm_2 \dots - M_n dm_n \geq 0. \quad (137)$$

That is, the temperature of the body must be equal to  $T$ , and the potentials of its components must satisfy the same conditions as if it were in contact and in equilibrium with a body having potentials  $M_1, M_2, \dots M_n$ . Therefore the same relations must subsist between  $\mu_a \dots \mu_g$  and  $M_1 \dots M_n$  as between the units of the corresponding substances, so that

$$m_a \mu_a \dots + m_g \mu_g = m_1 M_1 \dots + m_n M_n; \quad (138)$$

and as we have by (93)

$$\varepsilon = t \eta - p v + \mu_a m_a \dots + \mu_g m_g, \quad (139)$$

the expression (133) will reduce (for the body or bodies for which it has the least value per unit of volume) to

$$(P - p) v, \quad (140)$$

the value of which will be positive, null, or negative, according as the value of

$$P - p \quad (141)$$

is positive, null, or negative.

Hence, the conditions in regard to the stability of a fluid of which all the ultimate components are independently variable admit a very simple expression. If the pressure of the fluid is greater than that of any other phase of the same components which has the same temperature and the same values of the potentials for its actual components, the fluid is stable without coexistent phases; if its pressure is not as great as that of some other such phase, it will be unstable; if its pressure is as great as that of any other such phase, but not greater than that of every other, the fluid will certainly not be unstable, and in all probability it will be stable (when enclosed in a rigid envelop which is impermeable to heat and to all kinds of matter), but it will be one of a set of coexistent phases of which the others are the phases which have the same pressure.

The considerations of the last two pages, by which the tests relating to the stability of a fluid are simplified, apply to such bodies as actually exist. But if we should form arbitrarily any equation as a fundamental equation, and ask whether a fluid of which the proper-

ties were given by that equation would be stable, the tests of stability last given would be insufficient, as some of our assumptions might not be fulfilled by the equation. The test, however, as first given (pages 156–159) would in all cases be sufficient.

*Stability in respect to Continuous Changes of Phase.*

In considering the changes which may take place in any mass, we have already had occasion to distinguish between infinitesimal changes in existing phases, and the formation of entirely new phases. A phase of a fluid may be stable in regard to the former kind of change, and unstable in regard to the latter. In this case it may be capable of continued existence in virtue of properties which prevent the commencement of discontinuous changes. But a phase which is unstable in regard to continuous changes is evidently incapable of permanent existence on a large scale except in consequence of passive resistances to change. We will now consider the conditions of stability in respect to continuous changes of phase, or, as it may also be called, stability in respect to adjacent phases. We may use the same general test as before, except that the expression (133) is to be applied only to phases which differ infinitely little from the phase of which the stability is in question. In this case the component substances to be considered will be limited to the independently variable components of the fluid, and the constants  $M_1, M_2$ , etc. must have the values of the potentials for these components in the given fluid. The constants in (133) are thus entirely determined and the value of the expression for the given phase is necessarily zero. If for any infinitely small variation of the phase, the value of (133) can become negative, the fluid will be unstable; but if for every infinitely small variation of the phase the value of (133) becomes positive, the fluid will be stable. The only remaining case, in which the phase can be varied without altering the value of (133) can hardly be expected to occur. The phase concerned would in such a case have coexistent adjacent phases. It will be sufficient to discuss the condition of stability (in respect to continuous changes) without coexistent adjacent phases.

This condition, which for brevity's sake we will call the condition of stability, may be written in the form

$$\varepsilon'' - t' \eta'' + p' v'' - \mu_1' m_1'' \dots - \mu_n' m_n'' > 0, \quad (142)$$

in which the quantities relating to the phase of which the stability is in question are distinguished by single accents, and those relating to

the other phase by double accents. This condition is by (93) equivalent to

$$\begin{aligned} \varepsilon'' - t' \eta'' + p' v'' - \mu_1' m_1'' \dots - \mu_n' m_n'' \\ - \varepsilon' + t' \eta' - p' v' + \mu_1' m_1' \dots + \mu_n' m_n' > 0, \end{aligned} \quad (143)$$

and to

$$\begin{aligned} -t' \eta'' + p' v'' - \mu_1' m_1'' \dots - \mu_n' m_n'' \\ + t'' \eta'' - p'' v'' + \mu_1'' m_1'' \dots + \mu_n'' m_n'' > 0. \end{aligned} \quad (144)$$

The condition (143) may be expressed more briefly in the form

$$\Delta \varepsilon > t \Delta \eta - p \Delta v + \mu_1 \Delta m_1 \dots + \mu_n \Delta m_n, \quad (145)$$

if we use the character  $\Delta$  to signify that the condition, although relating to infinitesimal differences, is not to be interpreted in accordance with the usual convention in respect to differential equations with neglect of infinitesimals of higher orders than the first, but is to be interpreted *strictly*, like an equation between finite differences. In fact, when a condition like (145) (interpreted strictly) is satisfied for infinitesimal differences, it must be possible to assign limits within which it shall hold true of finite differences. But it is to be remembered that the condition is not to be applied to any arbitrary values of  $\Delta \eta$ ,  $\Delta v$ ,  $\Delta m_1$ , . . .  $\Delta m_n$ , but only to such as are determined by a change of phase. (If only the quantity of the body which determines the value of the variables should vary and not its phase, the value of the first member of (145) would evidently be zero.) We may free ourselves from this limitation by making  $v$  constant, which will cause the term  $-p \Delta v$  to disappear. If we then divide by the constant  $v$ , the condition will become

$$\frac{\Delta \varepsilon}{v} > t \frac{\Delta \eta}{v} + \mu_1 \frac{\Delta m_1}{v} \dots + \mu_n \frac{\Delta m_n}{v}, \quad (146)$$

in which form it will not be necessary to regard  $v$  as constant. As we may obtain from (86)

$$d \frac{\varepsilon}{v} = t d \frac{\eta}{v} + \mu_1 d \frac{m_1}{v} \dots + \mu_n d \frac{m_n}{v}, \quad (147)$$

we see that *the stability of any phase in regard to continuous changes depends upon the same conditions in regard to the second and higher differential coefficients of the density of energy regarded as a function of the density of entropy and the densities of the several components, which would make the density of energy a minimum, if the necessary conditions in regard to the first differential coefficients were fulfilled.* When  $n=1$ , it may be more convenient to regard  $m$  as constant

in (145) than  $v$ . Regarding  $m$  a constant, it appears that the stability of a phase depends upon the same conditions in regard to the second and higher differential coefficients of the energy of a unit of mass regarded as a function of its entropy and volume, which would make the energy a minimum, if the necessary conditions in regard to the first differential coefficients were fulfilled.

The formula (144) expresses the condition of stability for the phase to which  $t'$ ,  $p'$ , etc. relate. But it is evidently the necessary and sufficient condition of the stability of all phases of certain kinds of matter, or of all phases within given limits, that (144) shall hold true of any two infinitesimally differing phases within the same limits, or, as the case may be, in general. For the purpose, therefore, of such *collective* determinations of stability, we may neglect the distinction between the two states compared, and write the condition in the form

$$-\eta \Delta t + v \Delta p - m_1 \Delta \mu_1 \dots - m_n \Delta \mu_n > 0, \quad (148)$$

or

$$\Delta p > \frac{\eta}{v} \Delta t + \frac{m_1}{v} \Delta \mu_1 \dots + \frac{m_n}{v} \Delta \mu_n. \quad (149)$$

Comparing (98), we see that it is necessary and sufficient for the stability in regard to continuous changes of all the phases within any given limits, that within those limits the same conditions should be fulfilled in respect to the second and higher differential coefficients of the pressure regarded as a function of the temperature and the several potentials, which would make the pressure a minimum, if the necessary conditions with respect to the first differential coefficients were fulfilled.

By equations (87) and (94), the condition (142) may be brought to the form

$$\begin{aligned} & \psi'' + t'' \eta'' + p' v'' - \mu_1' m_1'' \dots - \mu_n' m_n'' \\ & - \psi' - t' \eta' - p' v' + \mu_1' m_1' \dots + \mu_n' m_n' > 0. \end{aligned} \quad (150)$$

For the stability of all phases within any given limits it is necessary and sufficient that within the same limits this condition shall hold true of any two phases which differ infinitely little. This evidently requires that when  $v' = v''$ ,  $m_1' = m_1''$ ,  $\dots$   $m_n' = m_n''$ ,

$$\psi'' - \psi' + (t'' - t') \eta'' > 0; \quad (151)$$

and that when  $t' = t''$

$$\begin{aligned} & \psi'' + p' v'' - \mu_1' m_1'' \dots + \mu_n' m_n'' \\ & - \psi' - p' v' + \mu_1' m_1' \dots + \mu_n' m_n' > 0. \end{aligned} \quad (152)$$

These conditions may be written in the form



$$[\Delta\psi + \eta \Delta t]_{v,m} < 0, \quad (153)$$

$$[\Delta\psi + p \Delta v - \mu_1 \Delta m_1 \dots - \mu_n \Delta m_n]_t > 0, \quad (154)$$

in which the subscript letters indicate the quantities which are to be regarded as constant,  $m$  standing for all the quantities  $m_1 \dots m_n$ . If these conditions hold true within any given limits, (150) will also hold true of any two infinitesimally differing phases within the same limits. To prove this, we will consider a third phase, determined by the equations

$$t''' = t', \quad (155)$$

and

$$v''' = v'', \quad m_1''' = m_1'', \quad \dots \quad m_n''' = m_n''. \quad (156)$$

Now by (153),

$$\psi''' - \psi'' + (t''' - t'') \eta'' < 0; \quad (157)$$

and by (154),

$$\begin{aligned} & \psi''' + p' v''' - \mu_1' m_1''' \dots - \mu_n' m_n''' \\ & - \psi'' - p' v'' + \mu_1' m_1'' \dots + \mu_n' m_n'' > 0. \end{aligned} \quad (158)$$

Hence,

$$\begin{aligned} & \psi'' + t'' \eta'' + p' v''' - \mu_1' m_1''' \dots - \mu_n' m_n''' \\ & - \psi' - t''' \eta'' - p' v' + \mu_1' m_1' \dots + \mu_n' m_n' > 0, \end{aligned} \quad (159)$$

which by (155) and (156) is equivalent to (150). Therefore, the conditions (153) and (154) in respect to the phases within any given limits are necessary and sufficient for the stability of all the phases within those limits. It will be observed that in (153) we have the condition of thermal stability of a body considered as unchangeable in composition and in volume, and in (154), the condition of mechanical and chemical stability of the body considered as maintained at a constant temperature. Comparing equation (88), we see that the condition (153) will be satisfied, if  $\frac{d^2\psi}{dt^2} < 0$ , i. e., if  $\frac{d\eta}{dt}$  or  $t\frac{d\eta}{dt}$  (the specific heat for constant volume) is positive. When  $n = 1$ , i. e., when the composition of the body is invariable, the condition (154) will evidently not be altered, if we regard  $m$  as constant, by which the condition will be reduced to

$$[\Delta\psi + p \Delta v]_{t,m} > 0. \quad (160)$$

This condition will evidently be satisfied if  $\frac{d^2\psi}{dv^2} > 0$ , i. e., if  $-\frac{dp}{dv}$  or  $-v\frac{dp}{dv}$  (the elasticity for constant temperature) is positive. But when  $n > 1$ , (154) may be abbreviated more symmetrically by making  $v$  constant.

Again, by (91) and (96), the condition (142) may be brought to the form

$$\begin{aligned} & \zeta'' + t'' \eta'' - p'' v'' - \mu_1' m_1'' \dots - \mu_n' m_n'' \\ & - \zeta' - t' \eta' + p' v' + \mu_1' m_1' \dots + \mu_n' m_n' > 0. \end{aligned} \quad (161)$$

Therefore, for the stability of all phases within any given limits it is necessary and sufficient that within the same limits

$$[\Delta \zeta + \eta \Delta t - v \Delta p]_m < 0, \quad (162)$$

and

$$[\Delta \zeta - \mu_1 \Delta m_1 \dots - \mu_n \Delta m_n]_{t,p} > 0, \quad (163)$$

as may easily be proved by the method used with (153) and (154). The first of these formulæ expresses the thermal and mechanical conditions of stability for a body considered as unchangeable in composition, and the second the conditions of chemical stability for a body considered as maintained at a constant temperature and pressure. If  $n=1$ , the second condition falls away, and as in this case  $\zeta = m\mu$ , condition (162) becomes identical with (148).

The foregoing discussion will serve to illustrate the relation of the general condition of stability in regard to continuous changes to some of the principal forms of fundamental equations. It is evident that each of the conditions (146), (149), (154), (162), (163) involve in general several particular conditions of stability. We will now give our attention to the latter. Let

$$\Phi = \varepsilon - t' \eta + p' v - \mu_1' m_1 \dots - \mu_n' m_n, \quad (164)$$

the accented letters referring to one phase and the unaccented to another. It is by (142) the necessary and sufficient condition of the stability of the first phase that, for constant values of the quantities relating to that phase and of  $v$ , the value of  $\Phi$  shall be a minimum when the second phase is identical with the first. Differentiating (164), we have by (86)

$$\begin{aligned} d\Phi = (t - t') d\eta - (p - p') dv + (\mu_1 - \mu_1') dm_1 \\ \dots - (\mu_n - \mu_n') dm_n. \end{aligned} \quad (165)$$

Therefore, the above condition requires that if we regard  $v, m_1, \dots, m_n$  as having the constant values indicated by accenting these letters,  $t$  shall be an increasing function of  $\eta$ , when the variable phase differs sufficiently little from the fixed. But as the fixed phase may be any one within the limits of stability,  $t$  must be an increasing function of  $\eta$  (within these limits) for any constant values of  $v, m_1, \dots, m_n$ . This condition may be written

$$\left( \frac{\Delta t}{\Delta \eta} \right)_{v, m_1, \dots, m_n} > 0. \quad (166)$$

When this condition is satisfied, the value of  $\Phi$ , for any given values of  $v, m_1, \dots m_n$ , will be a minimum when  $t = t'$ . And therefore, in applying the general condition of stability relating to the value of  $\Phi$ , we need only consider the phases for which  $t = t'$ .

We see again by (165) that the general condition requires that if we regard  $t, v, m_2, \dots m_n$  as having the constant values indicated by accenting these letters,  $\mu_1$  shall be an increasing function of  $m_1$ , when the variable phase differs sufficiently little from the fixed. But as the fixed phase may be any one within the limits of stability,  $\mu_1$  must be an increasing function of  $m_1$  (within these limits) for any constant values of  $t, v, m_2, \dots m_n$ . That is,

$$\left(\frac{\Delta\mu_1}{\Delta m_1}\right)_{t, v, m_2, \dots m_n} > 0. \quad (167)$$

When this condition is satisfied, as well as (166),  $\Phi$  will have a minimum value, for any constant values of  $v, m_2, \dots m_n$ , when  $t = t'$  and  $\mu_1 = \mu_1'$ ; so that in applying the general condition of stability we need only consider the phases for which  $t = t'$  and  $\mu_1 = \mu_1'$ .

In this way we may also obtain the following particular conditions of stability:

$$\left(\frac{\Delta\mu_2}{\Delta m_2}\right)_{t, v, m_1, m_3, \dots m_n} > 0, \quad (168)$$

. . . . .

$$\left(\frac{\Delta\mu_n}{\Delta m_n}\right)_{t, v, m_1, \dots m_{n-1}} > 0. \quad (169)$$

When the  $n + 1$  conditions (166)–(169) are all satisfied, the value of  $\Phi$ , for any constant value of  $v$ , will be a minimum when the temperature and the potentials of the variable phase are equal to those of the fixed. The pressures will then also be equal and the phases will be entirely identical. Hence, the general condition of stability will be completely satisfied, when the above particular conditions are satisfied.

From the manner in which these particular conditions have been derived, it is evident that we may interchange in them  $\eta, m_1, \dots m_n$  in any way, provided that we also interchange in the same way  $t, \mu_1, \dots \mu_n$ . In this way we may obtain different sets of  $n + 1$  conditions which are necessary and sufficient for stability. The quantity  $v$  might be included in the first of these lists, and  $-p$  in the second, except in cases when, in some of the phases considered, the entropy or the quantity of one of the components has the value zero.





Let us write  $R_{n+1}$  for the determinant of the order  $n + 1$

$$\begin{vmatrix} \frac{d^2 \varepsilon}{d\eta^2} & \frac{d^2 \varepsilon}{dm_1 d\eta} & \cdots & \frac{d^2 \varepsilon}{dm_n d\eta} \\ \frac{d^2 \varepsilon}{d\eta dm_1} & \frac{d^2 \varepsilon}{dm_1^2} & \cdots & \frac{d^2 \varepsilon}{dm_n dm_1} \\ \vdots & \vdots & \ddots & \vdots \\ \frac{d^2 \varepsilon}{d\eta dm_n} & \frac{d^2 \varepsilon}{dm_1 dm_n} & \cdots & \frac{d^2 \varepsilon}{dm_n^2} \end{vmatrix} \quad (173)$$

of which the constituents are by (86) the same as the coefficients in equations (172), and  $R_n, R_{n-1}$ , etc. for the minors obtained by erasing the last column and row in the original determinant and in the minors successively obtained, and  $R_1$  for the last remaining constituent. Then if  $dt, d\mu_1, \dots, d\mu_{n-1}$ , and  $dv$  all have the value zero, we have by (172)

$$R_n d\mu_n = R_{n+1} dm_n, \quad (174)$$

that is,

$$\left( \frac{d\mu_n}{dm_n} \right)_{t, v, \mu_1, \dots, \mu_{n-1}} = \frac{R_{n+1}}{R_n}. \quad (175)$$

In like manner we obtain

$$\left( \frac{d\mu_{n-1}}{dm_{n-1}} \right)_{t, v, \mu_1, \dots, \mu_{n-2}, m_n} = \frac{R_n}{R_{n-1}}, \quad (176)$$

etc.

Therefore, the conditions obtained by writing  $d$  for  $\Delta$  in (166)–(169) are equivalent to this, that the determinant given above with the  $n$  minors obtained from it as above mentioned and the last remaining constituent  $\frac{d^2 \varepsilon}{d\eta^2}$  shall all be positive. Any phase for which this condition is satisfied will be stable, and no phase will be stable for which any of these quantities has a negative value. But the conditions (166)–(169) will remain valid, if we interchange in any way  $\eta, m_1, \dots, m_n$  (with corresponding interchange of  $t, \mu_1, \dots, \mu_n$ ). Hence the order in which we erase successive columns with the corresponding rows in the determinant is immaterial. Therefore none of the minors of the determinant (173) which are formed by erasing corresponding rows and columns, and none of the constituents of the principal diagonal, can be negative for a stable phase.

We will now consider the conditions which characterize the *limits of stability* (i. e., the limits which divide stable from unstable phases)

with respect to continuous changes.\* Here, evidently, one of the conditions (166)–(169) must cease to hold true. Therefore, one of the differential coefficients formed by changing  $\mathcal{A}$  into  $d$  in the first members of these conditions must have the value zero. (That it is the numerator and not the denominator in the differential coefficient which vanishes at the limit appears from the consideration that the denominator is in each case the differential of a quantity which is necessarily capable of progressive variation, so long at least as the phase is capable of variation at all under the conditions expressed by the subscript letters.) The same will hold true of the set of differential coefficients obtained from these by interchanging in any way  $\eta, m_1, \dots m_n$ , and simultaneously interchanging  $t, \mu_1, \dots \mu_n$  in the same way. But we may obtain a more definite result than this.

Let us give to  $\eta$  or  $t$ , to  $m_1$  or  $\mu_1, \dots$  to  $m_{n-1}$  or  $\mu_{n-1}$ , and to  $v$ , the constant values indicated by these letters when accented. Then by (165)

$$d\Phi = (\mu_n - \mu_n') dm_n. \quad (177)$$

Now

$$\mu_n - \mu_n' = \left( \frac{d\mu_n}{dm_n} \right)' (m_n - m_n') \quad (178)$$

approximately, the differential coefficient being interpreted in accordance with the above assignment of constant values to certain variables, and its value being determined for the phase to which the accented letters refer. Therefore,

$$d\Phi = \left( \frac{d\mu_n}{dm_n} \right)' (m_n - m_n') dm_n, \quad (179)$$

and

$$\Phi = \frac{1}{2} \left( \frac{d\mu_n}{dm_n} \right)' (m_n - m_n')^2. \quad (180)$$

The quantities neglected in the last equation are evidently of the same order as  $(m_n - m_n')^3$ . Now this value of  $\Phi$  will of course be different (the differential coefficient having a different meaning) according as we have made  $\eta$  or  $t$  constant, and according as we have made  $m_1$  or  $\mu_1$  constant, etc.; but since, within the limits of stability, the value of  $\Phi$ , for any constant values of  $m_n$  and  $v$ , will be the least when  $t, p, \mu_1, \dots \mu_{n-1}$  have the values indicated by accenting these letters, the value of the differential coefficient will be at least as small

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\* The limits of stability with respect to discontinuous changes are formed by phases which are coexistent with other phases. Some of the properties of such phases have already been considered. See pages 152–156.

when we give these variables these constant values, as when we adopt any other of the suppositions mentioned above in regard to the quantities remaining constant. And in all these relations we may interchange in any way  $\eta, m_1, \dots m_n$ , if we interchange in the same way  $t, \mu_1, \dots \mu_n$ . It follows that, within the limits of stability, when we choose for any one of the differential coefficients

$$\frac{dt}{d\eta}, \frac{d\mu_1}{dm_1}, \dots \frac{d\mu_n}{dm_n} \quad (181)$$

the quantities following the sign  $d$  in the numerators of the others together with  $v$  as those which are to remain constant in differentiation, the value of the differential coefficient as thus determined will be at least as small as when one or more of the constants in differentiation are taken from the denominators, one being still taken from each fraction, and  $v$  as before being constant.

Now we have seen that none of these differential coefficients, as determined in any of these ways, can have a negative value within the limit of stability, and that some of them must have the value zero at that limit. Therefore, in virtue of the relations just established, one at least of these differential coefficients determined by considering constant the quantities occurring in the numerators of the others together with  $v$ , will have the value zero. But if one such has the value zero, all such will in general have the same value. For if

$$\left( \frac{d\mu_n}{dm_n} \right)_{t, v, \mu_1, \dots \mu_{n-1}} \quad (182)$$

for example, has the value zero, we may change the density of the component  $S_n$  without altering (if we disregard infinitesimals of higher orders than the first) the temperature or the potentials, and therefore, by (98), without altering the pressure. That is, we may change the phase without altering any of the quantities  $t, p, \mu_1, \dots \mu_n$ . (In other words, the phases adjacent to the limits of stability exhibit *approximately* the relations characteristic of neutral equilibrium.) Now this change of phase, which changes the density of one of the components, will in general change the density of the others and the density of entropy. Therefore, all the other differential coefficients formed after the analogy of (182), i. e., formed from the fractions in (181) by taking as constants for each the quantities in the numerators of the others together with  $v$ , will in general have the value zero at the limit of stability. And the relation which characterizes the limit of stability may be expressed, in general, by setting any one of these differential coefficients equal to zero. Such

an equation, when the fundamental equation is known, may be reduced to the form of an equation between the independent variables of the fundamental equation.

Again, as the determinant (173) is equal to the product of the differential coefficients obtained by writing  $d$  for  $\Delta$  in the first members of (166)–(169), the equation of the limit of stability may be expressed by setting this determinant equal to zero. The form of the differential equation as thus expressed will not be altered by the interchange of the expressions  $\eta, m_1, \dots m_n$ , but it will be altered by the substitution of  $v$  for any one of these expressions, which will be allowable whenever the quantity for which it is substituted has not the value zero in any of the phases to which the formula is to be applied.

The condition formed by setting the expression (182) equal to zero is evidently equivalent to this, that

$$\left\{ \frac{d\mu_n}{d\frac{m_n}{v}} \right\}_{t, \mu_1, \dots \mu_{n-1}} = 0, \quad (183)$$

that is, that

$$\left\{ \frac{d\frac{m_n}{v}}{d\mu_n} \right\}_{t, \mu_1, \dots \mu_{n-1}} = \infty, \quad (184)$$

or by (98), if we regard  $t, \mu_1, \dots \mu_n$  as the independent variables,

$$\left( \frac{d^2 p}{d\mu_n^2} \right) = \infty. \quad (185)$$

In like manner we may obtain

$$\frac{d^2 p}{dt^2} = \infty, \quad \frac{d^2 p}{d\mu_1^2} = \infty, \dots \frac{d^2 p}{d\mu_{n-1}^2} = \infty. \quad (186)$$

Any one of these equations, (185), (186), may be regarded, in general, as the equation of the limit of stability. We may be certain that at every phase at that limit one at least of these equations will hold true.

#### GEOMETRICAL ILLUSTRATIONS.

##### *Surfaces in which the Composition of the Body represented is Constant.*

In vol. ii, p. 382, of the Trans. Conn. Acad., a method is described of representing the thermodynamic properties of substances of invariable composition by means of surfaces. The volume, entropy, and energy



of a constant quantity of a substance are represented by rectangular co-ordinates. This method corresponds to the first kind of fundamental equation described on pages 140–144. Any other kind of fundamental equation for a substance of invariable composition will suggest an analogous geometrical method. Thus, if we make  $m$  constant, the variables in any one of the sets (99)–(103) are reduced to three, which may be represented by rectangular co-ordinates. This will, however, afford but four different methods, for, as has already (page 150) been observed, the two last sets are essentially equivalent when  $n = 1$ .

The method described in the preceding volume has certain advantages, especially for the purposes of theoretical discussion, but it may often be more advantageous to select a method in which the properties represented by two of the co-ordinates shall be such as best serve to identify and describe the different states of the substance. This condition is satisfied by temperature and pressure as well, perhaps, as by any other properties. We may represent these by two of the co-ordinates and the potential by the third. (See page 143.) It will not be overlooked that there is the closest analogy between these three quantities in respect to their parts in the general theory of equilibrium. (A similar analogy exists between volume, entropy, and energy.) If we give  $m$  the constant value unity, the third co-ordinate will also represent  $\zeta$ , which then becomes equal to  $\mu$ .

Comparing the two methods, we observe that in one

$$v = x, \quad \eta = y, \quad \varepsilon = z, \quad (187)$$

$$p = -\frac{dz}{dx}, \quad t = \frac{dz}{dy}, \quad \mu = \zeta = z - \frac{dz}{dx}x - \frac{dz}{dy}y; \quad (188)$$

and in the other

$$t = x, \quad p = y, \quad \mu = \zeta = z, \quad (189)$$

$$\eta = -\frac{dz}{dx}, \quad v = \frac{dz}{dy}, \quad \varepsilon = z - \frac{dz}{dx}x - \frac{dz}{dy}y. \quad (190)$$

Now  $\frac{dz}{dx}$  and  $\frac{dz}{dy}$  are evidently determined by the inclination of the tangent plane, and  $z - \frac{dz}{dx}x - \frac{dz}{dy}y$  is the segment which it cuts off on the axis of  $Z$ . The two methods, therefore, have this reciprocal relation, that the quantities represented in one by the position of a point in a surface are represented in the other by the position of a tangent plane.

The surfaces defined by equations' (187) and (189) may be distinguished as the  $v$ - $\eta$ - $\varepsilon$  surface, and the  $t$ - $p$ - $\zeta$  surface, of the substance to which they relate.

In the  $t$ - $p$ - $\zeta$  surface a line in which one part of the surface cuts another represents a series of pairs of coexistent states. A point through which pass three different parts of the surface represents a triad of coexistent states. Through such a point will evidently pass the three lines formed by the intersection of these sheets taken two by two. The perpendicular projection of these lines upon the  $p$ - $t$  plane will give the curves which have recently been discussed by Professor J. Thomson.\* These curves divide the space about the projection of the triple point into six parts which may be distinguished as follows: Let  $\zeta^{(V)}$ ,  $\zeta^{(L)}$ ,  $\zeta^{(S)}$  denote the three ordinates determined for the same values of  $p$  and  $t$  by the three sheets passing through the triple point, then in one of the six spaces

$$\zeta^{(V)} < \zeta^{(L)} < \zeta^{(S)}, \quad (191)$$

in the next space, separated from the former by the line for which  $\zeta^{(L)} = \zeta^{(S)}$ ,

$$\zeta^{(V)} < \zeta^{(S)} < \zeta^{(L)}, \quad (192)$$

in the third space, separated from the last by the line for which  $\zeta^{(V)} = \zeta^{(S)}$ ,

$$\zeta^{(S)} < \zeta^{(V)} < \zeta^{(L)}, \quad (193)$$

in the fourth  $\zeta^{(S)} < \zeta^{(L)} < \zeta^{(V)}$ , (194)

in the fifth  $\zeta^{(L)} < \zeta^{(S)} < \zeta^{(V)}$ , (195)

in the sixth  $\zeta^{(L)} < \zeta^{(V)} < \zeta^{(S)}$ . (196)

The sheet which gives the least values of  $\zeta$  is in each case that which represents the stable states of the substance. From this it is evident that in passing around the projection of the triple point we pass through lines representing alternately coexistent stable and coexistent unstable states. But the states represented by the intermediate values of  $\zeta$  may be called stable *relatively* to the states represented by the highest. The differences  $\zeta^{(L)} - \zeta^{(V)}$ , etc. represent the amount of work obtained in bringing the substance by a reversible process from one to the other of the states to which these quantities relate, in a medium having the temperature and pressure common to the two states. To illustrate such a process, we may suppose a plane perpendicular to the axis of temperature to pass through the points

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\* See the Reports of the British Association for 1871 and 1872; and Philosophical Magazine, vol. xlvii. (1874), p. 447.

representing the two states. This will in general cut the double line formed by the two sheets to which the symbols ( $L$ ) and ( $V$ ) refer. The intersections of the plane with the two sheets will connect the double point thus determined with the points representing the initial and final states of the process, and thus form a *reversible path* for the body between those states.

The geometrical relations which indicate the stability of any state may be easily obtained by applying the principles stated on pp. 156 ff. to the case in which there is but a single component. The expression (133) as a test of stability will reduce to

$$\varepsilon - t' \eta + p' v - \mu' m, \quad (197)$$

the accented letters referring to the state of which the stability is in question, and the unaccented letters to any other state. If we consider the quantity of matter in each state to be unity, this expression may be reduced by equations (91) and (96) to the form

$$\zeta - \zeta' + (t - t') \eta - (p - p') v, \quad (198)$$

which evidently denotes the distance of the point ( $t', p', \zeta'$ ) below the tangent plane for the point ( $t, p, \zeta$ ), measured parallel to the axis of  $\zeta$ . Hence if the tangent plane for every other state passes above the point representing any given state, the latter will be stable. If any of the tangent planes pass below the point representing the given state, that state will be unstable. Yet it is not always necessary to consider these tangent planes. For, as has been observed on page 160, we may assume that (in the case of any real substance) there will be at least one not unstable state for any given temperature and pressure, except when the latter is negative. Therefore the state represented by a point in the surface on the positive side of the plane  $p = 0$  will be unstable only when there is a point in the surface for which  $t$  and  $p$  have the same values and  $\zeta$  a less value. It follows from what has been stated, that where the surface is doubly convex upwards (in the direction in which  $\zeta$  is measured) the states represented will be stable in respect to adjacent states. This also appears directly from (162). But where the surface is concave upwards in either of its principal curvatures the states represented will be unstable in respect to adjacent states.

When the number of component substances is greater than unity, it is not possible to represent the fundamental equation by a single surface. We have therefore to consider how it may be represented by an infinite number of surfaces. A natural extension of either of the methods already described will give us a series of surfaces in

which every one is the  $v$ - $\eta$ - $\epsilon$  surface, or every one the  $t$ - $p$ - $\zeta$  surface for a body of constant composition, the proportion of the components varying as we pass from one surface to another. But for a simultaneous view of the properties which are exhibited by compounds of two or three components without change of temperature or pressure, we may more advantageously make one or both of the quantities  $t$  or  $p$  constant in each surface.

*Surfaces and Curves in which the Composition of the Body represented is Variable and its Temperature and Pressure are Constant.*

When there are three components, the position of a point in the  $X$ - $Y$  plane may indicate the composition of a body most simply, perhaps, as follows. The body is supposed to be composed of the quantities  $m_1, m_2, m_3$  of the substances  $S_1, S_2, S_3$ , the value of  $m_1 + m_2 + m_3$  being unity. Let  $P_1, P_2, P_3$  be any three points in the plane, which are not in the same straight line. If we suppose masses equal to  $m_1, m_2, m_3$  to be placed at these three points, the center of gravity of these masses will determine a point which will indicate the value of these quantities. If the triangle is equiangular and has the height unity, the distances of the point from the three sides will be equal numerically to  $m_1, m_2, m_3$ . Now if for every possible phase of the components, of a given temperature and pressure, we lay off from the point in the  $X$ - $Y$  plane which represents the composition of the phase a distance measured parallel to the axis of  $Z$  and representing the value of  $\zeta$  (when  $m_1 + m_2 + m_3 = 1$ ), the points thus determined will form a surface, which may be designated as the  $m_1$ - $m_2$ - $m_3$ - $\zeta$  surface of the substances considered, or simply as their  $m$ - $\zeta$  surface, for the given temperature and pressure. In like manner, when there are but two component substances, we may obtain a curve, which we will suppose in the  $X$ - $Z$  plane. The coordinate  $y$  may then represent temperature or pressure. But we will limit ourselves to the consideration of the properties of the  $m$ - $\zeta$  surface for  $n = 3$ , or the  $m$ - $\zeta$  curve for  $n = 2$ , regarded as a surface, or curve, which varies with the temperature and pressure.

As by (96) and (92)

$$\zeta = \mu_1 m_1 + \mu_2 m_2 + \mu_3 m_3,$$

and (for constant temperature and pressure)

$$d\zeta = \mu_1 dm_1 + \mu_2 dm_2 + \mu_3 dm_3,$$

if we imagine a tangent plane for the point to which these letters relate, and denote by  $\zeta'$  the ordinate for any point in the plane,



and by  $m_1', m_2', m_3'$ , the distances of the foot of this ordinate from the three sides of the triangle  $P_1 P_2 P_3$ , we may easily obtain

$$\zeta' = \mu_1 m_1' + \mu_2 m_2' + \mu_3 m_3', \quad (199)$$

which we may regard as the equation of the tangent plane. Therefore the ordinates for this plane at  $P_1, P_2$ , and  $P_3$  are equal respectively to the potentials  $\mu_1, \mu_2$ , and  $\mu_3$ . And in general, the ordinate for any point in the tangent plane is equal to the potential (in the phase represented by the point of contact) for a substance of which the composition is indicated by the position of the ordinate. (See page 149.) Among the bodies which may be formed of  $S_1, S_2$ , and  $S_3$ , there may be some which are incapable of variation in composition, or which are capable only of a single kind of variation. These will be represented by single points and curves in vertical planes. Of the tangent plane to one of these curves only a single line will be fixed, which will determine a series of potentials of which only two will be independent. The phase represented by a separate point will determine only a single potential, viz., the potential for the substance of the body itself, which will be equal to  $\zeta$ .

The points representing a set of coexistent phases have in general a common tangent plane. But when one of these points is situated on the edge where a sheet of the surface terminates, it is sufficient if the plane is tangent to the edge and passes below the surface. Or, when the point is at the end of a separate line belonging to the surface, or at an angle in the edge of a sheet, it is sufficient if the plane pass through the point and below the line or sheet. If no part of the surface lies below the tangent plane, the points where it meets the plane will represent a stable (or at least not unstable) set of coexistent phases.

The surface which we have considered represents the relation between  $\zeta$  and  $m_1, m_2, m_3$  for homogeneous bodies when  $t$  and  $p$  have any constant values and  $m_1 + m_2 + m_3 = 1$ . It will often be useful to consider the surface which represents the relation between the same variables for bodies which consist of parts in different but coexistent phases. We may suppose that these are stable, at least in regard to adjacent phases, as otherwise the case would be devoid of interest. The point which represents the state of the composite body will evidently be at the center of gravity of masses equal to the parts of the body placed at the points representing the phases of these parts. Hence from the surface representing the properties of homogeneous bodies, which may be called the primitive surface, we

may easily construct the surface representing the properties of bodies which are in equilibrium but not homogeneous. This may be called the secondary or derived surface. It will consist, in general, of various portions or sheets. The sheets which represent a combination of two phases may be formed by rolling a double tangent plane upon the primitive surface: the part of the envelop of its successive positions which lies between the curves traced by the points of contact will belong to the derived surface. When the primitive surface has a triple tangent plane or one of higher order, the triangle in the tangent plane formed by joining the points of contact, or the smallest polygon without re-entrant angles which includes all the points of contact, will belong to the derived surface, and will represent masses consisting in general of three or more phases.

Of the whole thermodynamic surface as thus constructed for any temperature and any positive pressure, that part is especially important which gives the least value of  $\zeta$  for any given values of  $m_1$ ,  $m_2$ ,  $m_3$ . The state of a mass represented by a point in this part of the surface is one in which no dissipation of energy would be possible if the mass were enclosed in a rigid envelop impermeable both to matter and to heat; and the state of any mass composed of  $S_1$ ,  $S_2$ ,  $S_3$  in any proportions, in which the dissipation of energy has been completed, so far as internal processes are concerned, (i. e., under the limitations imposed by such an envelop as above supposed,) would be represented by a point in the part which we are considering of the  $m$ - $\zeta$  surface for the temperature and pressure of the mass. We may therefore briefly distinguish this part of the surface as the *surface of dissipated energy*. It is evident that it forms a continuous sheet, the projection of which upon the  $X$ - $Y$  plane coincides with the triangle  $P_1 P_2 P_3$ , (except when the pressure for which the  $m$ - $\zeta$  surface is constructed is negative, in which case there is no surface of dissipated energy,) that it nowhere has any convexity upward, and that the states which it represents are in no case unstable.

The general properties of the  $m$ - $\zeta$  lines for two component substances are so similar as not to require separate consideration. We now proceed to illustrate the use of both the surfaces and the lines by the discussion of several particular cases.

Three coexistent phases of two component substances may be represented by the points A, B, and C, in figure 1, in which  $\zeta$  is measured toward the top of the page from  $P_1 P_2$ ,  $m_1$  toward the left from  $P_2 Q_2$ , and  $m_2$  toward the right from  $P_1 Q_1$ . It is supposed that  $P_1 P_2 = 1$ . Portions of the curves to which these points belong

are seen in the figure, and will be denoted by the symbols (A), (B), (C). We may, for convenience, speak of these as separate curves, without implying anything in regard to their possible continuity in parts of the diagram remote from their common tangent AC. The *line of dissipated energy* includes the straight line AC and portions of the primitive curves (A) and (C). Let us first consider how the

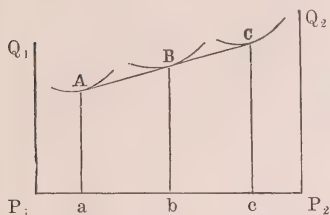


FIG. 1.

diagram will be altered, if the temperature is varied while the pressure remains constant. If the temperature receives the increment  $dt$ , an ordinate of which the position is fixed will receive the increment  $\left(\frac{d\zeta}{dt}\right)_{p,m} dt$ , or  $-\eta dt$ . (The reader will easily convince himself that this is true of the

ordinates for the secondary line AC, as well as of the ordinates for the primitive curves.) Now if we denote by  $\eta'$  the entropy of the phase represented by the point B considered as belonging to the curve (B), and by  $\eta''$  the entropy of the composite state of the same matter represented by the point B considered as belonging to the tangent to the curves (A) and (C),  $t(\eta' - \eta'')$  will denote the heat yielded by a unit of matter in passing from the first to the second of these states. If this quantity is positive, an elevation of temperature will evidently cause a part of the curve (B) to protrude below the tangent to (A) and (C), which will no longer form a part of the line of dissipated energy. This line will then include portions of the three curves (A), (B), and (C), and of the tangents to (A) and (B) and to (B) and (C). On the other hand, a lowering of the temperature will cause the curve (B) to lie entirely above the tangent to (A) and (C), so that all the phases of the sort represented by (B) will be unstable. If  $t(\eta' - \eta'')$  is negative, these effects will be produced by the opposite changes of temperature.

The effect of a change of pressure while the temperature remains constant may be found in a manner entirely analogous. The variation of any ordinate will be  $\left(\frac{d\zeta}{dp}\right)_{t,m} dp$  or  $v dp$ . Therefore, if the volume of the homogeneous phase represented by the point B is a greater than the volume of the same matter divided between the the phases represented by A and C, an increase of pressure will give diagram indicating that all phases of the sort represented by curve (B) are unstable, and a decrease of pressure will give a diagram indi-

cating two stable pairs of coexistent phases, in each of which one of the phases is of the sort represented by the curve (B). When the relation of the volumes is the reverse of that supposed, these results will be produced by the opposite changes of pressure.

When we have four coexistent phases of three component substances, there are two cases which must be distinguished. In the first, one of the points of contact of the primitive surface with the quadruple tangent plane lies within the triangle formed by joining the other three; in the second, the four points may be joined so as to form a quadrilateral without re-entrant angles. Figure 2 represents the projection upon the  $X-Y$  plane (in which  $m_1, m_2, m_3$  are measured) of a part of the surface of dissipated energy, when one of the points of contact D falls within the triangle formed by the other three A, B, C. This surface includes the triangle ABC in the quadruple tangent plane, portions of the three sheets of the primitive surface which touch the triangle at its vertices, EAF, GBH, ICK, and portions of the three developable surfaces formed by a tangent plane rolling upon each pair of these sheets. These developable surfaces are repre-

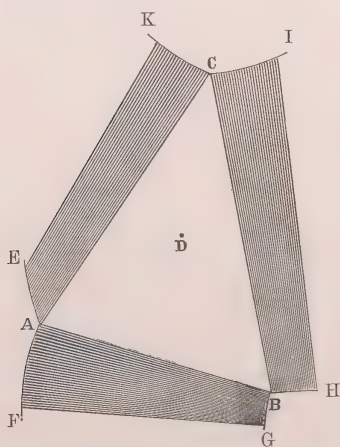


FIG. 2.

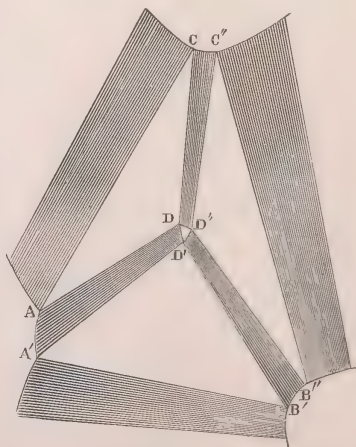


FIG. 3.

sented in the figure by ruled surfaces, the lines indicating the direction of their rectilinear elements. A point within the triangle ABC represents a mass of which the matter is divided, in general, between three or four different phases, in a manner not entirely determined by the position of a point. (The quantities of matter in these phases are such that if placed at the corresponding points, A, B, C, D, their center of gravity would be at the point representing the total mass.)



Such a mass, if exposed to constant temperature and pressure, would be in neutral equilibrium. A point in the developable surfaces represents a mass of which the matter is divided between two coexisting phases, which are represented by the extremities of the line in the figure passing through that point. A point in the primitive surface represents of course a homogeneous mass.

To determine the effect of a change of temperature without change of pressure upon the general features of the surface of dissipated energy, we must know whether heat is absorbed or yielded by a mass in passing from the phase represented by the point D *in the primitive surface* to the composite state consisting of the phases A, B, and C which is represented by the same point. If the first is the case, an increase of temperature will cause the sheet (D) (i. e., the sheet of the primitive surface to which the point D belongs) to separate from the plane tangent to the three other sheets, so as to be situated entirely above it, and a decrease of temperature, will cause a part of the sheet (D) to protrude through the plane tangent to the other sheets. These effects will be produced by the opposite changes of temperature, when heat is yielded by a mass passing from the homogeneous to the composite state above mentioned.

In like manner, to determine the effect of a variation of pressure without change of temperature, we must know whether the volume for the homogeneous phase represented by D is greater or less than the volume of the same matter divided between the phases A, B, and C. If the homogeneous phase has the greater volume, an increase of pressure will cause the sheet (D) to separate from the plane tangent to the other sheets, and a diminution of pressure will cause a part of the sheet (D) to protrude below that tangent plane. And these effects will be produced by the opposite changes of pressure, if the homogeneous phase has the less volume. All this appears from precisely the same considerations which were used in the analogous case for two component substances.

Now when the sheet (D) rises above the plane tangent to the other sheets, the general features of the surface of dissipated energy are not altered, except by the disappearance of the point D. But when the sheet (D) protrudes below the plane tangent to the other sheets, the surface of dissipated energy will take the form indicated in figure 3. It will include portions of the four sheets of the primitive surface, portions of the six developable surfaces formed by a double tangent plane rolling upon these sheets taken two by two, and portions of three triple tangent planes for these sheets taken by threes, the sheet (D) being always one of the three.

But when the points of contact with the quadruple tangent plane which represent the four coexistent phases can be joined so as to form a quadrilateral ABCD (fig. 4) without reentrant angles, the surface of dissipated energy will include this plane quadrilateral, portions of the four sheets of the primitive surface which are tangent to it, and portions of the four developable surfaces formed by double

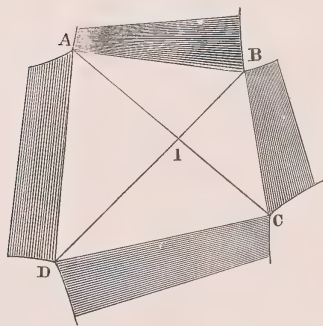


FIG. 4.

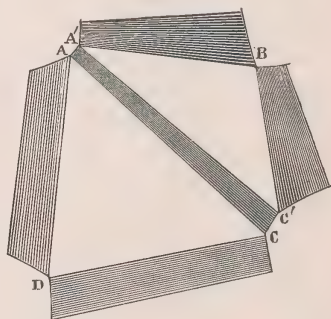


FIG. 5.

tangent planes rolling upon the four pairs of these sheets which correspond to the four sides of the quadrilateral. To determine the general effect of a variation of temperature upon the surface of dissipated energy, let us consider the composite states represented by the point I at the intersection of the diagonals of the quadrilateral. Among these states (which all relate to the same kind and quantity of matter) there is one which is composed of the phases A and C, and another which is composed of the phases B and D. Now if the entropy of the first of these states is greater than that of the second, (i. e., if heat is given out by a body in passing from the first to the second state at constant temperature and pressure,) which we may suppose without loss of generality, an elevation of temperature while the pressure remains constant will cause the triple tangent planes to (B), (D), and (A), and to (B), (D), and (C), to rise above the triple tangent planes to (A), (C), and (B), and to (A), (C), and (D), in the vicinity of the point I. The surface of dissipated energy will therefore take the form indicated in figure 5, in which there are two plane triangles and five developable surfaces besides portions of the four primitive sheets. A diminution of temperature will give a different but entirely analogous form to the surface of dissipated energy. The quadrilateral ABCD will in this case break into two triangles along the diameter BD. The effects produced by

variation of the pressure while the temperature remains constant will of course be similar to those described. By considering the difference of volume instead of the difference of entropy of the two states represented by the point I in the quadruple tangent plane, we may distinguish between the effects of increase and diminution of pressure.

It should be observed that the points of contact of the quadruple tangent plane with the primitive surface may be at isolated points or curves belonging to the latter. So also, in the case of two component substances, the points of contact of the triple tangent line may be at isolated points belonging to the primitive curve. Such cases need not be separately treated, as the necessary modifications in the preceding statements, when applied to such cases, are quite evident. And in the remaining discussion of this geometrical method, it will generally be left to the reader to make the necessary limitations or modifications in analogous cases.

The necessary condition in regard to simultaneous variations of temperature and pressure, in order that four coexistent phases of three components, or three coexistent phases of two components, shall remain possible, has already been deduced by purely analytical processes. (See equation (129).)

We will next consider the case of two coexistent phases of identical composition, and first, when the number of components is two. The coexistent phases, if each is variable in composition, will be represented by the point of contact of two curves. One of the curves will in general lie above the other except at the point of contact; therefore, when the temperature and pressure remain constant, one phase cannot be varied in composition without becoming unstable, while the other phase will be stable if the proportion of either component is increased. By varying the temperature or pressure, we may cause the upper curve to protrude below the other, or to rise (relatively) entirely above it. (By comparing the volumes or the entropies of the two coexistent phases, we may easily determine which result would be produced by an increase of temperature or of pressure.) Hence, the temperatures and pressures for which two coexistent phases have the same composition form the limit to the temperatures and pressures for which such coexistent phases are possible. It will be observed that as we pass this limit of temperature and pressure, the pair of coexistent phases does not simply become unstable, like pairs and triads of coexistent phases which we have considered before, but there ceases to be any such pair of coexistent phases. The same result has already been obtained analytically on

page 155. But on that side of the limit on which the coexistent phases are possible, there will be two pairs of coexistent phases for the same values of  $t$  and  $p$ , as seen in figure 6. If the curve  $AA'$  represents vapor, and the curve  $BB'$  liquid, a liquid

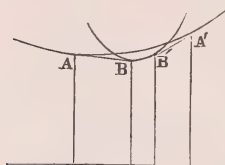


FIG. 6.

(represented by) B may exist in contact with a vapor A, and (at the same temperature and pressure) a liquid B' in contact with a vapor A'. If we compare these phases in respect to their composition, we see that in one case the vapor is richer than the liquid in a certain component, and in the other case poorer. Therefore, if these liquids are made to boil, the effect on their composition will be opposite. If the boiling is continued under constant pressure, the temperature will rise as the liquids approach each other in composition, and the curve  $BB'$  will rise *relatively* to the curve  $AA'$ , until the curves are tangent to each other, when the two liquids become identical in nature, as also the vapors which they yield. In composition, and in the value of  $\zeta$  per unit of mass, the vapor will then agree with the liquid. But if the curve  $BB'$  (which has the greater curvature) represents vapor, and  $AA'$  represents liquid, the effect of boiling will make the liquids A and A' differ more in composition. In this case, the relations indicated in the figure will hold for a temperature higher than that for which (with the same pressure) the curves are tangent to one another.

When two coexistent phases of three component substances have the same composition, they are represented by the point of contact of two sheets of the primitive surface. If these sheets do not intersect at the point of contact, the case is very similar to that which we have just considered. The upper sheet except at the point of contact represents unstable phases. If the temperature or pressure are so varied that a part of the upper sheet protrudes through the lower, the points of contact of a double tangent plane rolling upon the two sheets will describe a closed curve on each, and the surface of dissipated energy will include a portion of each sheet of the primitive surface united by a ring-shaped developable surface.

If the sheet having the greater curvatures represents liquid, and the other sheet vapor, the boiling temperature for any given pressure will be a maximum, and the pressure of saturated vapor for any given temperature will be a minimum, when the coexistent liquid and vapor have the same composition.

But if the two sheets, constructed for the temperature and pressure of the coexistent phases which have the same composition, intersect



at the point of contact, the whole primitive surface as seen from below will in general present four re-entrant furrows, radiating from the point of contact, for each of which a developable surface may be formed by a rolling double tangent plane. The different parts of the surface of dissipated energy in the vicinity of the point of contact are represented in figure 7. ATB, ETF are parts of one sheet of the primitive surface, and CTD, GTH are parts of the other. These are united by the developable surfaces BTC, DTE, FTG, HTA. Now we may make either sheet of the primitive surface sink relatively to the other by the proper variation of temperature or pressure. If the sheet to which ATB, ETF belong is that which sinks relatively, these

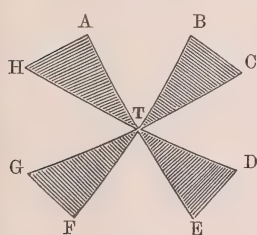


FIG. 7.

parts of the surface of dissipated energy will be merged in one, as well as the developable surfaces BTC, DTE, and also FTG, HTA. (The lines CTD, BTE, ATF, HTG will separate from one another at T, each forming a continuous curve.) But if the sheet of the primitive surface which sinks relatively is that to which CTD and GTH belong, then these parts will be merged in one in the surface of dissipated energy, as will be the developable surfaces BTC, ATH, and also DTE, FTG.

It is evident that this is not a case of maximum or minimum temperature for coexistent phases under constant pressure, or of maximum or minimum pressure for coexistent phases at constant temperature.

Another case of interest is when the composition of one of three coexistent phases is such as can be produced by combining the other two. In this case, the primitive surface must touch the same plane in three points in the same straight line. Let us distinguish the parts of the primitive surface to which these points belong as the sheets (A), (B), and (C), (C) denoting that which is intermediate in position. The sheet (C) is evidently tangent to the developable surface formed upon (A) and (B). It may or it may not intersect it at the point of contact. If it does not, it must lie above the developable surface, (unless it represents states which are unstable in regard to continuous changes,) and the surface of dissipated energy will include parts of the primitive sheets (A) and (B), the developable surface joining them, and the single point of the sheet (C) in which it meets this developable surface. Now, if the temperature or pressure is varied so as to make the sheet (C) rise above the

developable surface formed on the sheets (A) and (B), the surface of dissipated energy will be altered in its general features only by the removal of the single point of the sheet (C). But if the temperature or pressure is altered so as to make a part of the sheet (C) protrude through the developable surface formed on (A) and (B), the surface

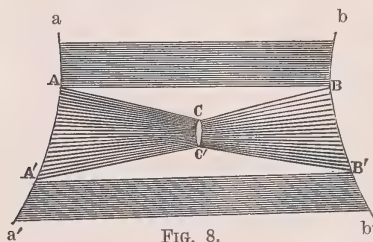


FIG. 8.

of dissipated energy will have the form indicated in figure 8. It will include two plane triangles ABC and A'B'C', a part of each of the sheets (A) and (B), represented in the figure by the spaces on the left of the line aAA'a' and on the right of the line bBB'b', a small part CC' of the sheet (C), and developable surfaces formed upon these sheets taken by pairs ACC'A', BCC'B', aABb, a'A'B'b', the last two being different portions of the same developable surface.

But if, when the primitive surface is constructed for such a temperature and pressure that it has three points of contact with the same plane in the same straight line, the sheet (C) (which has the middle position) at its point of contact with the triple tangent plane intersects the developable surface formed upon the other sheets (A) and (B), the surface of dissipated energy will not include this developable surface, but will consist of portions of the three primitive sheets with two developable surfaces formed on (A) and (C) and on (B) and (C). These developable surfaces meet one another at the point of contact of (C) with the triple tangent plane, dividing the

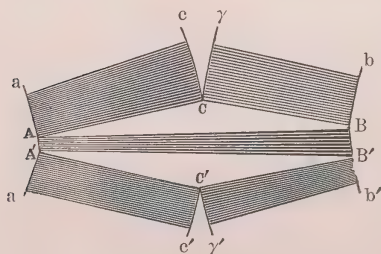


FIG. 9.

portion of this sheet which belongs to the surface of dissipated energy into two parts. If now the temperature or pressure are varied so as to make the sheet (C) sink relatively to the developable surface formed on (A) and (B), the only alteration in the general features of the surface of dissipated energy will be that the developable surfaces

formed on (A) and (C) and on (B) and (C) will separate from one another, and the two parts of the sheet (C) will be merged in one. But a contrary variation of temperature or pressure will give a

surface of dissipated energy such as is represented in figure (9), containing two plane triangles  $ABC$ ,  $A'B'C'$  belonging to triple tangent planes, a portion of the sheet (A) on the left of the line  $aAA'a'$ , a portion of the sheet (B) on the right of the line  $bBB'b'$ , two separate portions  $cC\gamma$  and  $c'C'\gamma'$  of the sheet (C), two separate portions  $aACc$  and  $a'A'C'e'$  of the developable surface formed on (A) and (C), two separate portions  $bBC\gamma$  and  $b'B'C'\gamma'$  of the developable surface formed on (B) and (C), and the portion  $A'ABB'$  of the developable surface formed on (A) and (B).

From these geometrical relations it appears that (in general) the temperature of three coexistent phases is a maximum or minimum for constant pressure, and the pressure of three coexistent phases a maximum or minimum for constant temperature, when the composition of the three coexistent phases is such that one can be formed by combining the other two. This result has been obtained analytically on page 156.

The preceding examples are amply sufficient to illustrate the use of the  $m$ - $\zeta$  surfaces and curves. The physical properties indicated by the nature of the surface of dissipated energy have been only occasionally mentioned, as they are often far more distinctly indicated by the diagrams than they could be in words. It will be observed that a knowledge of the lines which divide the various different portions of the surface of dissipated energy and of the direction of the rectilinear elements of the developable surfaces, *as projected upon the  $X$ - $Y$  plane*, without a knowledge of the form of the  $m$ - $\zeta$  surface in space, is sufficient for the determination (in respect to the quantity and composition of the resulting masses) of the combinations and separations of the substances, and of the changes in their states of aggregation, which take place when the substances are exposed to the temperature and pressure to which the projected lines relate, except so far as such transformations are prevented by passive resistances to change.

#### CRITICAL PHASES.

It has been ascertained by experiment that the variations of two coexistent states of the same substance are in some cases limited in one direction by a terminal state at which the distinction of the coexistent states vanishes.\* This state has been called the *critical state*. Analogous properties may doubtless be exhibited by compounds of variable composition without change of temperature or

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\* See Dr. Andrews "On the continuity of the gaseous and liquid states of matter." *Phil. Trans.*, vol. 159, p. 575.

pressure. For if, at any given temperature and pressure, two liquids are capable of forming a stable mixture in any ratio  $m_1 : m_2$  less than  $a$ , and in any greater than  $b$ ,  $a$  and  $b$  being the values of that ratio for two coexistent phases, while either can form a stable mixture with a third liquid in all proportions, and any small quantities of the first and second can unite at once with a great quantity of the third to form a stable mixture, it may easily be seen that two coexistent mixtures of the three liquids may be varied in composition, the temperature and pressure remaining the same, from initial phases in each of which the quantity of the third liquid is nothing, to a terminal phase in which the distinction of the two phases vanishes.

In general, we may define a *critical phase* as one at which the distinction between coexistent phases vanishes. We may suppose the coexistent phases to be stable in respect to continuous changes, for although relations in some respects analogous might be imagined to hold true in regard to phases which are unstable in respect to continuous changes, the discussion of such cases would be devoid of interest. But if the coexistent phases and the critical phase are unstable only in respect to the possible formation of phases entirely different from the critical and adjacent phases, the liability to such changes will in no respect affect the relations between the critical and adjacent phases, and need not be considered in a theoretical discussion of these relations, although it may prevent an experimental realization of the phases considered. For the sake of brevity, in the following discussion, phases in the vicinity of the critical phase will generally be called stable, if they are unstable only in respect to the formation of phases entirely different from any in the vicinity of the critical phase.

Let us first consider the number of independent variations of which a critical phase (while remaining such) is capable. If we denote by  $n$  the number of independently variable components, a pair of coexistent phases will be capable of  $n$  independent variations, which may be expressed by the variations of  $n$  of the quantities  $t, p, \mu_1, \mu_2, \dots, \mu_n$ . If we limit these variations by giving to  $n-1$  of the quantities the constant values which they have for a certain critical phase, we obtain a linear\* series of pairs of coexistent phases terminated by the critical phase. If we now vary infinitesimally the values of these  $n-1$  quantities, we shall have for the new set of values considered constant a new linear series of pairs of coexistent phases. Now for every pair of phases in the first series, there must be pairs of phases in the

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\* This term is used to characterize a series having a *single* degree of extension.



second series differing infinitely little from the pair in the first, and *vice versa*, therefore the second series of coexistent phases must be terminated by a critical phase which differs, but differs infinitely little, from the first. We see, therefore, that if we vary arbitrarily the values of any  $n-1$  of the quantities  $t, p, \mu_1, \mu_2, \dots \mu_n$ , as determined by a critical phase, we obtain one and only one critical phase for each set of varied values; i. e., a critical phase is capable of  $n-1$  independent variations.

The quantities  $t, p, \mu_1, \mu_2, \dots \mu_n$  have the same values in two coexistent phases, but the ratios of the quantities  $\eta, v, m_1, m_2, \dots m_n$ , are in general different in the two phases. Or, if for convenience we compare equal volumes of the two phases (which involves no loss of generality), the quantities  $\eta, m_1, m_2, \dots m_n$  will in general have different values in two coexistent phases. Applying this to coexistent phases indefinitely near to a critical phase, we see that in the immediate vicinity of a critical phase, if the values of  $n$  of the quantities  $t, p, \mu_1, \mu_2, \dots \mu_n$  are regarded as constant (as well as  $v$ ), the variations of either of the others will be infinitely small compared with the variations of the quantities  $\eta, m_1, m_2, \dots m_n$ . This condition, which we may write in the form

$$\left( \frac{d\mu_n}{dm_n} \right)_{t, v, \mu_1, \dots \mu_{n-1}} = 0, \quad (200)$$

characterizes, as we have seen on page 171, the limits which divide stable from unstable phases in respect to continuous changes.

In fact, if we give to the quantities  $t, \mu_1, \mu_2, \dots \mu_{n-1}$  constant values determined by a pair of coexistent phases, and to  $\frac{m_n}{v}$  a series of values increasing from the less to the greater of the values which it has in these coexistent phases, we determine a linear series of phases connecting the coexistent phases, in some part of which  $\mu_n$ —since it has the same value in the two coexistent phases, but not a uniform value throughout the series (for if it had, which is theoretically improbable, all these phases would be coexistent)—must be a decreasing function of  $\frac{m_n}{v}$ , or of  $m_n$ , if  $v$  also is supposed constant. Therefore, the series must contain phases which are unstable in respect to continuous changes. (See page 168.) And as such a pair of coexistent phases may be taken indefinitely near to any critical phase, the unstable phases (with respect to continuous changes) must approach indefinitely near to this phase.

Critical phases have similar properties with reference to stability as determined with regard to discontinuous changes. For as every stable phase which has a coexistent phase lies upon the limit which separates stable from unstable phases, the same must be true of any stable critical phase. (The same may be said of critical phases which are unstable in regard to discontinuous changes if we leave out of account the liability to the particular kind of discontinuous change in respect to which the critical phase is unstable.)

The linear series of phases determined by giving to  $n$  of the quantities  $t, p, \mu_1, \mu_2, \dots \mu_n$  the constant values which they have in any pair of coexistent phases consists of unstable phases in the part between the coexistent phases, but in the part beyond these phases in either direction it consists of stable phases. Hence, if a critical phase is varied in such a manner that  $n$  of the quantities  $t, p, \mu_1, \mu_2, \dots \mu_n$  remain constant, it will remain stable in respect both to continuous and to discontinuous changes. Therefore,  $\mu_n$  is an increasing function of  $m_n$  when  $t, v, \mu_1, \mu_2, \dots \mu_{n-1}$  have constant values determined by any critical phase. But as equation (200) holds true at the critical phase, the following conditions must also hold true at that phase:

$$\left( \frac{d^2 \mu_n}{dm_n^2} \right)_{t, v, \mu_1, \dots \mu_{n-1}} = 0, \quad (201)$$

$$\left( \frac{d^3 \mu_n}{dm_n^3} \right)_{t, v, \mu_1, \dots \mu_{n-1}} \geq 0. \quad (202)$$

If the sign of equality holds in the last condition, additional conditions, concerning the differential coefficients of higher orders, must be satisfied.

Equations (200) and (201) may in general be called the equations of critical phases. It is evident that there are only two independent equations of this character, as a critical phase is capable of  $n-1$  independent variations.

We are not, however, absolutely certain that equation (200) will always be satisfied by a critical phase. For it is possible that the denominator in the fraction may vanish as well as the numerator for an infinitesimal change of phase in which the quantities indicated are constant. In such a case, we may suppose the subscript  $n$  to refer to some different component substance, or use another differential coefficient of the same general form (such as are described on page 171 as characterizing the limits of stability in respect to continuous changes), making the corresponding changes in (201) and (202). We may be certain that some of the formulæ thus formed will not fail. But for a perfectly rigorous method there is an advan-

tage in the use of  $\eta, v, m_1, m_2, \dots m_n$  as independent variables. The condition that the phase may be varied without altering any of the quantities  $t, \mu_1, \mu_2, \dots \mu_n$  will then be expressed by the equation

$$R_{n+1} = 0, \quad (203)$$

in which  $R_{n+1}$  denotes the same determinant as on page 169. To obtain the second equation characteristic of critical phases, we observe that as a phase which is critical cannot become unstable when varied so that  $n$  of the quantities  $t, p, \mu_1, \mu_2, \dots \mu_n$  remain constant, the differential of  $R_{n+1}$  for constant volume, viz.,

$$\frac{dR_{n+1}}{d\eta} d\eta + \frac{dR_{n+1}}{dm_1} dm_1 \dots + \frac{dR_{n+1}}{dm_n} dm_n \quad (204)$$

cannot become negative when  $n$  of the equations (172) are satisfied. Neither can it have a positive value, for then its value might become negative by a change of sign of  $d\eta, dm_1$ , etc. Therefore the expression (204) has the value zero, if  $n$  of the equations (172) are satisfied. This may be expressed by an equation

$$S = 0, \quad (205)$$

in which  $S$  denotes a determinant in which the constituents are the same as in  $R_{n+1}$ , except in a single horizontal line, in which the differential coefficients in (204) are to be substituted. In whatever line this substitution is made, the equation (205), as well as (203), will hold true of every critical phase without exception.

If we choose  $t, p, m_1, m_2, \dots m_n$  as independent variables, and write  $U$  for the determinant

$$\begin{vmatrix} \frac{d^2\zeta}{dm_1^2} & \frac{d^2\zeta}{dm_2 dm_1} & \dots & \frac{d^2\zeta}{dm_{n-1} dm_1} \\ \frac{d^2\zeta}{dm_1 dm_2} & \frac{d^2\zeta}{dm_2^2} & \dots & \frac{d^2\zeta}{dm_{n-1} dm_2} \\ \vdots & \vdots & \ddots & \vdots \\ \frac{d^2\zeta}{dm_1 dm_{n-1}} & \frac{d^2\zeta}{dm_2 dm_{n-1}} & \dots & \frac{d^2\zeta}{dm_{n-1}^2} \end{vmatrix} \quad (206)$$

and  $V$  for the determinant formed from this by substituting for the constituents in any horizontal line the expressions

$$\frac{dU}{dm_1}, \quad \frac{dU}{dm^2}, \quad \dots \quad \frac{dU}{dm_{n-1}}, \quad (207)$$

the equations of critical phases will be

$$U = 0, \quad V = 0. \quad (208)$$

It results immediately from the definition of a critical phase, that an infinitesimal change in the condition of a mass in such a phase

may cause the mass, if it remains in a state of dissipated energy (i. e., in a state in which the dissipation of energy by internal processes is complete), to cease to be homogeneous. In this respect a critical phase resembles any phase which has a coexistent phase, but differs from such phases in that the two parts into which the mass divides when it ceases to be homogeneous differ infinitely little from each other and from the original phase, and that neither of these parts is in general infinitely small. If we consider a change in the mass to be determined by the values of  $d\eta$ ,  $dv$ ,  $dm_1$ ,  $dm_2$ , . . .  $dm_n$ , it is evident that the change in question will cause the mass to cease to be homogeneous whenever the expression

$$\frac{dR_{n+1}}{d\eta} d\eta + \frac{dR_{n+1}}{dv} dv + \frac{dR_{n+1}}{dm_1} dm_1 + \dots + \frac{dR_{n+1}}{dm_n} dm_n \quad (209)$$

has a negative value. For if the mass should remain homogeneous, it would become unstable, as  $R_{n+1}$  would become negative. Hence, in general, any change thus determined, or its reverse (determined by giving to  $d\eta$ ,  $dv$ ,  $dm_1$ ,  $dm_2$ , . . .  $dm_n$  the same values taken negatively), will cause the mass to cease to be homogeneous. The condition which must be satisfied with reference to  $d\eta$ ,  $dv$ ,  $dm_1$ ,  $dm_2$ , . . .  $dm_n$ , in order that neither the change indicated, nor the reverse, shall destroy the homogeneity of the mass, is expressed by equating the above expression to zero.

But if we consider the change in the state of the mass (supposed to remain in a state of dissipated energy) to be determined by arbitrary values of  $n+1$  of the differentials  $dt$ ,  $dp$ ,  $d\mu_1$ ,  $d\mu_2$ , . . .  $d\mu_n$ , the case will be entirely different. For, if the mass ceases to be homogeneous, it will consist of two coexistent phases, and as applied to these only  $n$  of the quantities  $t$ ,  $p$ ,  $\mu_1$ ,  $\mu_2$ , . . .  $\mu_n$  will be independent. Therefore, for arbitrary variations of  $n+1$  of these quantities, the mass must in general remain homogeneous.

But if, instead of supposing the mass to remain in a state of dissipated energy, we suppose that it remains homogeneous, it may easily be shown that to certain values of  $n+1$  of the above differentials there will correspond three different phases, of which one is stable with respect both to continuous and to discontinuous changes, another is stable with respect to the former and unstable with respect to the latter, and the third is unstable with respect to both.

In general, however, if  $n$  of the quantities  $p$ ,  $t$ ,  $\mu_1$ ,  $\mu_2$ , . . .  $\mu_n$ , or  $n$  arbitrary functions of these quantities, have the same constant values as at a critical phase, the linear series of phases thus determined will be stable, in the vicinity of the critical phase. But if less



than  $n$  of these quantities or functions of the same together with certain of the quantities  $\eta, v, m_1, m_2, \dots m_n$ , or arbitrary functions of the latter quantities, have the same values as at a critical phase, so as to determine a linear series of phases, the differential of  $R_{n+1}$  in such a series of phases will not in general vanish at the critical phase, so that in general a part of the series will be unstable.

We may illustrate these relations by considering separately the cases in which  $n=1$  and  $n=2$ . If a mass of invariable composition is in a critical state, we may keep its volume constant, and destroy its homogeneity by changing its entropy (i. e., by adding or subtracting heat—probably the latter), or we may keep its entropy constant and destroy its homogeneity by changing its volume; but if we keep its pressure constant we cannot destroy its homogeneity by any thermal action, nor if we keep its temperature constant can we destroy its homogeneity by any mechanical action.

When a mass having two independently variable components is in a critical phase, and either its volume or its pressure is maintained constant, its homogeneity may be destroyed by a change of entropy or temperature. Or, if either its entropy or its temperature is maintained constant, its homogeneity may be destroyed by a change of volume or pressure. In both these cases it is supposed that the quantities of the components remain unchanged. But if we suppose both the temperature and the pressure to be maintained constant, the mass will remain homogeneous, however the proportion of the components be changed. Or, if a mass consists of two coexistent phases, one of which is a critical phase having two independently variable components, and either the temperature or the pressure of the mass is maintained constant, it will not be possible by mechanical or thermal means, or by changing the quantities of the components, to cause the critical phase to change into a pair of coexistent phases, so as to give three coexistent phases in the whole mass. The statements of this paragraph and of the preceding have reference only to infinitesimal changes.\*

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\* A brief abstract (which came to the author's notice after the above was in type) of a memoir by M. Duclaux, "Sur la séparation des liquides mélangés, etc." will be found in *Comptes Rendus*, vol. lxxxi. (1875), p. 815.

ON THE VALUES OF THE POTENTIALS WHEN THE QUANTITY OF ONE OF THE COMPONENTS IS VERY SMALL.

If we apply equation (97) to a homogeneous mass having two independently variable components  $S_1$  and  $S_2$ , and make  $t$ ,  $p$ , and  $m_1$  constant, we obtain

$$m_1 \left( \frac{d\mu_1}{dm_2} \right)_{t, p, m_1} + m_2 \left( \frac{d\mu_2}{dm_2} \right)_{t, p, m_1} = 0. \quad (210)$$

Therefore, for  $m_2=0$ , either

$$\left( \frac{d\mu_1}{dm_2} \right)_{t, p, m_1} = 0, \quad (211)$$

or

$$\left( \frac{d\mu_2}{dm_2} \right)_{t, p, m_1} = \infty. \quad (212)$$

Now, whatever may be the composition of the mass considered, we may always so choose the substance  $S_1$  that the mass shall consist solely of that substance, and in respect to any other variable component  $S_2$ , we shall have  $m_2=0$ . But equation (212) cannot hold true *in general* as thus applied. For it may easily be shown (as has been done with regard to the potential on pages 148, 149) that the value of a differential coefficient like that in (212) for any given mass, when the substance  $S_2$  (to which  $m_2$  and  $\mu_2$  relate) is determined, is independent of the particular substance which we may regard as the other component of the mass; so that, if equation (212) holds true when the substance denoted by  $S_1$  has been so chosen that  $m_2=0$ , it must hold true without such a restriction, which cannot generally be the case.

In fact, it is easy to prove directly that equation (211) will hold true of any phase which is stable in regard to continuous changes and in which  $m_2=0$ , *if  $m_2$  is capable of negative as well as positive values*. For by (171), in any phase having that kind of stability,  $\mu_1$  is an increasing function of  $m_1$  when  $t$ ,  $p$ , and  $m_2$  are regarded as constant. Hence,  $\mu_1$  will have its greatest value when the mass consists wholly of  $S_1$ , i. e., when  $m_2=0$ . Therefore, if  $m_2$  is capable of negative as well as positive values, equation (211) must hold true for  $m_2=0$ . (This appears also from the geometrical representation of potentials in the  $m$ - $\mu$  curve. See page 177.)

But if  $m_2$  is capable only of positive values, we can only conclude from the preceding considerations that the value of the differential coefficient in (211) cannot be positive. Nor, if we consider the physical significance of this case, viz., that an increase of  $m_2$  denotes an

addition to the mass in question of a substance not before contained in it, does any reason appear for supposing that this differential coefficient has generally the value zero. To fix our ideas, let us suppose that  $S_1$  denotes water, and  $S_2$  a salt (either anhydrous or any particular hydrate). The addition of the salt to water, previously in a state capable of equilibrium with vapor or with ice, will destroy the possibility of such equilibrium at the same temperature and pressure. The liquid will dissolve the ice, or condense the vapor, which is brought in contact with it under such circumstances, which shows that  $\mu_1$  (the potential for water in the liquid mass) is diminished by the addition of the salt, when the temperature and pressure are maintained constant. Now there seems to be no *a priori* reason for supposing that the ratio of this diminution of the potential for water to the quantity of the salt which is added vanishes with this quantity. We should rather expect that, for small quantities of the salt, an effect of this kind would be proportional to its cause, i. e., that the differential coefficient in (211) would have a finite negative value for an infinitesimal value of  $m_2$ . That this is the case with respect to numerous watery solutions of salts is distinctly indicated by the experiments of Wüllner\* on the tension of the vapor yielded by such solutions, and of Rüdorff† on the temperature at which ice is formed in them; and unless we have experimental evidence that cases are numerous in which the contrary is true, it seems not unreasonable to assume, as a *general* law, that when  $m_2$  has the value zero and is incapable of negative values, the differential coefficient in (211) will have a finite negative value, and that equation (212) will therefore hold true. But this case must be carefully distinguished from that in which  $m_2$  is capable of negative values, which also may be illustrated by a solution of a salt in water. For this purpose let  $S_1$  denote a hydrate of the salt which can be crystallized, and let  $S_2$  denote water, and let us consider a liquid consisting entirely of  $S_1$  and of such temperature and pressure as to be in equilibrium with crystals of  $S_1$ . In such a liquid, an increase or a diminution of the quantity of water would alike cause crystals of  $S_1$  to dissolve, which requires that the differential coefficient in (211) shall vanish at the particular phase of the liquid for which  $m_2 = 0$ .

Let us return to the case in which  $m_2$  is incapable of negative values, and examine, without other restriction in regard to the substances

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\* Pogg. Ann., vol. ciii. (1858), p. 529; vol. cv. (1858), p. 85; vol. cx. (1860), p. 564.

† Pogg. Ann., vol. cxiv. (1861), p. 63.

denoted by  $S_1$  and  $S_2$ , the relation between  $\mu_2$  and  $\frac{m_2}{m_1}$  for any constant temperature and pressure and for such small values of  $\frac{m_2}{m_1}$  that the differential coefficient in (211) may be regarded as having the same constant value as when  $m_2 = 0$ , the values of  $t$ ,  $p$ , and  $m_1$  being unchanged. If we denote this value of the differential coefficient by  $\frac{-A}{m_1}$ , the value of  $A$  will be positive, and will be independent of  $m_1$ . Then for small values of  $\frac{m_2}{m_1}$ , we have by (210), approximately,

$$m_2 \left( \frac{d\mu_2}{dm_2} \right)_{t, p, m_1} = A, \quad (213)$$

i. e.,

$$\left( \frac{d\mu_2}{d \log m_2} \right)_{t, p, m_1} = A. \quad (214)$$

If we write the integral of this equation in the form

$$\mu_2 = A \log \frac{Bm_2}{m_1}, \quad (215)$$

$B$  like  $A$  will have a positive value depending only upon the temperature and pressure. As this equation is to be applied only to cases in which the value of  $m_2$  is very small compared with  $m_1$ , we may regard  $\frac{m_1}{v}$  as constant, when temperature and pressure are constant, and write

$$\mu_2 = A \log \frac{Cm_2}{v}, \quad (216)$$

$C$  denoting a positive quantity, dependent only upon the temperature and pressure.

We have so far considered the composition of the body as varying only in regard to the proportion of two components. But the argument will be in no respect invalidated, if we suppose the composition of the body to be capable of other variations. In this case, the quantities  $A$  and  $C$  will be functions not only of the temperature and pressure but also of the quantities which express the composition of the substance of which together with  $S_2$  the body is composed. If the quantities of any of the components besides  $S_2$  are very small (relatively to the quantities of others), it seems reasonable to assume that the value of  $\mu_2$ , and therefore the values of  $A$  and  $C$ , will be nearly the same as if these components were absent.



Hence, if the independently variable components of any body are  $S_a, \dots S_g$ , and  $S_h, \dots S_k$ , the quantities of the latter being very small as compared with the quantities of the former, and are incapable of negative values, we may express approximately the values of the potentials for  $S_h, \dots S_k$  by equations (subject of course to the uncertainties of the assumptions which have been made) of the form

$$\mu_h = A_h \log \frac{C_h m_h}{v}, \quad (217)$$

$$\mu_k = A_k \log \frac{C_k m_k}{v}, \quad (218)$$

in which  $A_h, C_h, \dots A_k, C_k$  denote functions of the temperature, the pressure, and the ratios of the quantities  $m_a, \dots m_g$ .

We shall see hereafter, when we come to consider the properties of gases, that these equations may be verified experimentally in a very large class of cases, so that we have considerable reason for believing that they express a general law in regard to the limiting values of potentials.\*

#### ON CERTAIN POINTS RELATING TO THE MOLECULAR CONSTITUTION OF BODIES.

It not unfrequently occurs that the number of proximate components which it is necessary to recognize as independently variable in a body exceeds the number of components which would be sufficient to express its ultimate composition. Such is the case, for example, as has been remarked on page 117, in regard to a mixture at ordinary temperatures of vapor of water and free hydrogen and oxygen. This case is explained by the existence of three sorts of molecules in the gaseous mass, viz., molecules of hydrogen, of oxygen, and of hydrogen and oxygen combined. In other cases, which are essentially the same in principle, we suppose a greater number of different sorts of molecules, which differ in composition, and the relations between

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\* The reader will not fail to remark that, if we could assume the universality of this law, the statement of the conditions necessary for equilibrium between different masses in contact would be much simplified. For, as the potential for a substance which is only a *possible* component (see page 117) would always have the value  $-\infty$ , the case could not occur that the potential for any substance should have a greater value in a mass in which that substance is only a possible component, than in another mass in which it is an actual component; and the conditions (22) and (51) might be expressed with the sign of equality without exception for the case of possible components.

these may be more complicated. Other cases are explained by molecules which differ in the quantity of matter which they contain, but not in the kind of matter, nor in the proportion of the different kinds. In still other cases, there appear to be different sorts of molecules, which differ neither in the kind nor in the quantity of matter which they contain, but only in the manner in which they are constituted. What is essential in the cases referred to is that a certain number of some sort or sorts of molecules shall be equivalent to a certain number of some other sort or sorts in respect to the kinds and quantities of matter which they collectively contain, and yet the former shall never be transformed into the latter within the body considered, nor the latter into the former, however the proportion of the numbers of the different sorts of molecules may be varied, or the composition of the body in other respects, or its thermodynamic state as represented by temperature and pressure or any other two suitable variables, provided, it may be, that these variations do not exceed certain limits. Thus, in the example given above, the temperature must not be raised beyond a certain limit, or molecules of hydrogen and of oxygen may be transformed into molecules of water.

The differences in bodies resulting from such differences in the constitution of their molecules are capable of continuous variation, in bodies containing the same matter and in the same thermodynamic state as determined, for example, by pressure and temperature, as the numbers of the molecules of the different sorts are varied. These differences are thus distinguished from those which depend upon the manner in which the molecules are combined to form sensible masses. The latter do not cause an increase in the number of variables in the fundamental equation; but they may be the cause of different values of which the function is sometimes capable for one set of values of the independent variables, as, for example, when we have several different values of  $\zeta$  for the same values of  $t$ ,  $p$ ,  $m_1$ ,  $m_2$ , . . .  $m_n$ , one perhaps being for a gaseous body, one for a liquid, one for an amorphous solid, and others for different kinds of crystals, and all being invariable for constant values of the above mentioned independent variables.

But it must be observed that when the differences in the constitution of the molecules are entirely determined by the quantities of the different kinds of matter in a body with the two variables which express its thermodynamic state, these differences will not involve any increase in the number of variables in the fundamental equation. For example, if we should raise the temperature of the mixture of

vapor of water and free hydrogen and oxygen, which we have just considered, to a point at which the numbers of the different sorts of molecules are entirely determined by the temperature and pressure and the total quantities of hydrogen and of oxygen which are present, the fundamental equation of such a mass would involve but four independent variables, which might be the four quantities just mentioned. The fact of a certain part of the matter present existing in the form of vapor of water would, of course, be one of the facts which determine the nature of the relation between  $\zeta$  and the independent variables, which is expressed by the fundamental equation.

But in the case first considered, in which the quantities of the different sorts of molecules are *not* determined by the temperature and pressure and the quantities of the different kinds of matter in the body as determined by its ultimate analysis, the components of which the quantities or the potentials appear in the fundamental equation must be those which are determined by the proximate analysis of the body, so that the variations in their quantities, with two variations relating to the thermodynamic state of the body, shall include all the variations of which the body is capable.\* Such cases present no especial difficulty; there is indeed nothing in the physical and chemical properties of such bodies, so far as a certain range of experiments is concerned, which is different from what might be, if the proximate components were incapable of farther reduction or transformation. Yet among the various phases of the kinds of matter concerned, represented by the different sets of values of the variables which satisfy the fundamental equation, there is a certain class which merit especial attention. These are the phases for which the entropy has a maximum value for the same matter, as determined by the ultimate analysis of the body, with the same energy and volume. To fix our ideas let us call the proximate components  $S_1, \dots S_n$ , and the ultimate components  $S_a, \dots S_k$ ; and let  $m_1, \dots m_n$  denote the quantities of the former, and  $m_a, \dots m_k$ , the quantities of the latter. It is evident that  $m_a \dots m_k$  are homogeneous functions of the first degree of  $m_1, \dots m_n$ ; and that the relations between the substances  $S_1, \dots S_n$  might be expressed by homogeneous equations of the first degree between the units of these substances, equal in number to the difference of the numbers of the proximate and of the ultimate com-

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\* The terms proximate or ultimate are not necessarily to be understood in an absolute sense. All that is said here and in the following paragraphs will apply to many cases in which components may conveniently be regarded as proximate or ultimate, which are such only in a relative sense.

ponents. The phases in question are those for which  $\eta$  is a maximum for constant values of  $\varepsilon$ ,  $v$ ,  $m_a, \dots m_h$ ; or, as they may also be described, those for which  $\varepsilon$  is a minimum for constant values of  $\eta$ ,  $v$ ,  $m_a, \dots m_h$ ; or for which  $\zeta$  is a minimum for constant values of  $t$ ,  $p$ ,  $m_a, \dots m_h$ . The phases which satisfy this condition may be readily determined when the fundamental equation (which will contain the quantities  $m_1, \dots m_n$  or  $\mu_1, \dots \mu_n$ ) is known. Indeed it is easy to see that we may express the conditions which determine these phases by substituting  $\mu_1, \dots \mu_n$  for the letters denoting the units of the corresponding substances in the equations which express the equivalence in ultimate analysis between these units.

These phases may be called, with reference to the kind of change which we are considering, phases of dissipated energy. That we have used a similar term before, with reference to a different kind of changes, yet in a sense entirely analogous, need not create confusion.

It is characteristic of these phases that we cannot alter the values of  $m_1, \dots m_n$  in any real mass in such a phase, while the volume of the mass as well as its matter remain unchanged, without diminishing the energy or increasing the entropy of some other system. Hence, if the mass is large, its equilibrium can be but slightly disturbed by the action of any small body, or by a single electric spark, or by any cause which is not in some way proportioned to the effect to be produced. But when the proportion of the proximate components of a mass taken in connection with its temperature and pressure is not such as to constitute a phase of dissipated energy, it may be possible to cause great changes in the mass by the contact of a very small body. Indeed it is possible that the changes produced by such contact may only be limited by the attainment of a phase of dissipated energy. Such a result will probably be produced in a fluid mass by contact with another fluid which contains molecules of all the kinds which occur in the first fluid (or at least all those which contain the same kinds of matter which also occur in other sorts of molecules), but which differs from the first fluid in that the quantities of the various kinds of molecules are entirely determined by the ultimate composition of the fluid and its temperature and pressure. Or, to speak without reference to the molecular state of the fluid, the result considered would doubtless be brought about by contact with another fluid, which absorbs all the proximate components of the first,  $S_1, \dots S_n$ , (or all those between which there exist relations of equivalence in respect to their ultimate analysis), independently, and without passive resistances, but for which the phase is completely deter-



mined by its temperature and pressure and its ultimate composition (in respect at least to the particular substances just mentioned). By the absorption of the substances  $S_1, \dots S_n$  independently and without passive resistances, it is meant that when the absorbing body is in equilibrium with another containing these substances, it shall be possible by *infinitesimal* changes in these bodies to produce the exchange of all these substances in either direction and independently. An exception to the preceding statement may of course be made for cases in which the result in question is prevented by the occurrence of some other kinds of change; in other words, it is assumed that the two bodies can remain in contact preserving the properties which have been mentioned.

The term *catalysis* has been applied to such action as we are considering. When a body has the property of reducing another, without limitation with respect to the proportion of the two bodies, to a phase of dissipated energy, in regard to a certain kind of molecular change, it may be called a *perfect catalytic agent* with respect to the second body and the kind of molecular change considered.

It seems not improbable that in some cases in which molecular changes take place slowly in homogeneous bodies, a mass of which the temperature and pressure are maintained constant will be finally brought to a state of equilibrium which is entirely determined by its temperature and pressure and the quantities of its ultimate components, while the various transitory states through which the mass passes, (which are evidently not completely defined by the quantities just mentioned,) may be completely defined by the quantities of certain proximate components with the temperature and pressure, and the matter of the mass may be brought by processes approximately reversible from permanent states to these various transitory states. In such cases, we may form a fundamental equation with reference to all possible phases, whether transitory or permanent; and we may also form a fundamental equation of different import and containing a smaller number of independent variables, which has reference solely to the final phases of equilibrium. The latter are the phases of dissipated energy (with reference to molecular changes), and when the more general form of the fundamental equation is known, it will be easy to derive from it the fundamental equation for these permanent phases alone.

Now, as these relations, theoretically considered, are independent of the rapidity of the molecular changes, the question naturally arises, whether in cases in which we are not able to distinguish such transi-

tory phases, they may not still have a theoretical significance. If so, the consideration of the subject from this point of view, may assist us, in such cases, in discovering the form of the fundamental equation with reference to the ultimate components, which is the only equation required to express all the properties of the bodies which are capable of experimental demonstration. Thus, when the phase of a body is completely determined by the quantities of  $n$  independently variable components, with the temperature and pressure, and we have reason to suppose that the body is composed of a greater number  $n'$  of proximate components, which are therefore not independently variable (while the temperature and pressure remain constant), it seems quite possible that the fundamental equation of the body may be of the same form as the equation for the phases of dissipated energy of analogous compounds of  $n'$  proximate and  $n$  ultimate components, in which the proximate components are capable of independent variation (without variation of temperature or pressure). And if such is found to be the case, the fact will be of interest as affording an indication concerning the proximate constitution of the body.

Such considerations seem to be especially applicable to the very common case in which at certain temperatures and pressures, regarded as constant, the quantities of certain proximate components of a mass are capable of independent variations, and all the phases produced by these variations are permanent in their nature, while at other temperatures and pressures, likewise regarded as constant, the quantities of these proximate components are not capable of independent variation, and the phase may be completely defined by the quantities of the ultimate components with the temperature and pressure. There may be, at certain intermediate temperatures and pressures, a condition with respect to the independence of the proximate components intermediate in character, in which the quantities of the proximate components are independently variable when we consider all phases, the essentially transitory as well as the permanent, but in which these quantities are not independently variable when we consider the permanent phases alone. Now we have no reason to believe that the passing of a body in a state of dissipated energy from one to another of the three conditions mentioned has any necessary connection with any discontinuous change of state. Passing the limit which separates one of these states from another will not therefore involve any discontinuous change in the values of any of the quantities enumerated in (99)–(103) on page 143, if  $m_1, m_2, \dots m_n, \mu_1, \mu_2, \dots \mu_n$  are

understood as always relating to the ultimate components of the body. Therefore, if we regard masses in the different conditions mentioned above as having different fundamental equations, (which we may suppose to be of any one of the five kinds described on page 143,) these equations will agree at the limits dividing these conditions not only in the values of all the variables which appear in the equations, but also in all the differential coefficients of the first order involving these variables. We may illustrate these relations by supposing the values of  $t$ ,  $p$ , and  $\zeta$  for a mass in which the quantities of the ultimate components are constant to be represented by rectilinear coordinates. Where the proximate composition of such a mass is not determined by  $t$  and  $p$ , the value of  $\zeta$  will not be determined by these variables, and the points representing connected values of  $t$ ,  $p$ , and  $\zeta$  will form a solid. This solid will be bounded in the direction opposite to that in which  $\zeta$  is measured, by a surface which represents the phases of dissipated energy. In a part of the figure, all the phases thus represented may be permanent, in another part only the phases in the bounding surface, and in a third part there may be no such solid figure (for any phases of which the existence is experimentally demonstrable), but only a surface. This surface together with the bounding surfaces representing phases of dissipated energy in the parts of the figure mentioned above forms a continuous sheet, without discontinuity in regard to the direction of its normal at the limits dividing the different parts of the figure which have been mentioned. (There may, indeed, be different sheets representing liquid and gaseous states, etc., but if we limit our consideration to states of one of these sorts, the case will be as has been stated.)

We shall hereafter, in the discussion of the fundamental equations of gases, have an example of the derivation of the fundamental equation for phases of dissipated energy (with respect to the molecular changes on which the proximate composition of the body depends) from the more general form of the fundamental equation.

#### THE CONDITIONS OF EQUILIBRIUM FOR HETEROGENEOUS MASSES UNDER THE INFLUENCE OF GRAVITY.

Let us now seek the conditions of equilibrium for a mass of various kinds of matter subject to the influence of gravity. It will be convenient to suppose the mass enclosed in an immovable envelop which is impermeable to matter and to heat, and in other respects, except in regard to gravity, to make the same suppositions as on pages 115, 116. The energy of the mass will now consist of two parts, one of

which depends upon its intrinsic nature and state, and the other upon its position in space. Let  $Dm$  denote an element of the mass,  $D\varepsilon$  the intrinsic energy of this element,  $h$  its height above a fixed horizontal plane, and  $g$  the force of gravity; then the total energy of the mass (when without sensible motions) will be expressed by the formula

$$\int D\varepsilon + \int g h Dm, \quad (219)$$

in which the integrations include all the elements of the mass; and the general condition of equilibrium will be

$$\delta \int D\varepsilon + \delta \int g h Dm \geq 0, \quad (220)$$

the variations being subject to certain equations of condition. These must express that the entropy of the whole mass is constant, that the surface bounding the whole mass is fixed, and that the total quantities of each of the component substances is constant. We shall suppose that there are no other equations of condition, and that the independently variable components are the same throughout the whole mass; and we shall at first limit ourselves to the consideration of the conditions of equilibrium with respect to the changes which may be expressed by infinitesimal variations of the quantities which define the initial state of the mass, without regarding the possibility of the formation at any place of infinitesimal masses entirely different from any initially existing in the same vicinity.

Let  $D\eta$ ,  $Dv$ ,  $Dm_1, \dots Dm_n$  denote the entropy of the element  $Dm$ , its volume, and the quantities which it contains of the various components. Then

$$Dm = Dm_1 \dots + Dm_n, \quad (221)$$

and

$$\delta Dm = \delta Dm_1 \dots + \delta Dm_n. \quad (222)$$

Also, by equation (12),

$$\delta D\varepsilon = t \delta D\eta - p \delta Dv + \mu_1 \delta Dm_1 \dots + \mu_n \delta Dm_n. \quad (223)$$

By these equations the general condition of equilibrium may be reduced to the form

$$\begin{aligned} & \int t \delta D\eta - \int p \delta Dv + \int \mu_1 \delta Dm_1 \dots + \int \mu_n \delta Dm_n \\ & + \int g \delta h Dm + \int g h \delta Dm_1 \dots + \int g h \delta Dm_n \geq 0. \end{aligned} \quad (224)$$

Now it will be observed that the different equations of condition affect different parts of this condition, so that we must have, separately,

$$\int t \delta D\eta \geq 0, \quad \text{if} \quad \int \delta D\eta = 0; \quad (225)$$



$$- \int p \delta Dv + \int g \delta h Dm \geq 0, \quad (226)$$

if the bounding surface is unvaried ;

$$\left. \begin{aligned} \int \mu_1 \delta Dm_1 + \int g h \delta Dm_1 &\geq 0, & \text{if } \int \delta Dm_1 &= 0 ; \\ \cdot &\cdot & \cdot &\cdot \\ \int \mu_n \delta Dm_n + \int g h \delta Dm_n &\geq 0, & \text{if } \int \delta Dm_n &= 0. \end{aligned} \right\} \quad (227)$$

From (225) we may derive the condition of thermal equilibrium,

$$t = \text{Const.} \quad (328)$$

Condition (226) is evidently the ordinary mechanical condition of equilibrium, and may be transformed by any of the usual methods. We may, for example, apply the formula to such motions as might take place longitudinally within an infinitely narrow tube, terminated at both ends by the external surface of the mass, but otherwise of indeterminate form. If we denote by  $m$  the mass, and by  $v$  the volume, included in the part of the tube between one end and a transverse section of variable position, the condition will take the form

$$- \int p \delta dv + \int g \delta h dm \geq 0, \quad (229)$$

in which the integrations include the whole contents of the tube. Since no motion is possible at the ends of the tube,

$$\int p \delta dv + \int \delta v dp = \int d(p \delta v) = 0. \quad (230)$$

Again, if we denote by  $\gamma$  the density of the fluid,

$$\int g \delta h dm = \int g \frac{dh}{dv} \delta v \gamma dv = \int g \gamma \delta v dh. \quad (231)$$

By these equations condition (229) may be reduced to the form

$$\int \delta v (dp + g \gamma dh) \geq 0. \quad (232)$$

Therefore, since  $\delta v$  is arbitrary in value,

$$dp = - g \gamma dh, \quad (233)$$

which will hold true at any point in the tube, the differentials being taken with respect to the direction of the tube at that point. Therefore, as the form of the tube is indeterminate, this equation must hold true, without restriction, throughout the whole mass. It evidently requires that the pressure shall be a function of the height alone, and that the density shall be equal to the first derivative of this function, divided by  $-g$ .

Conditions (227) contain all that is characteristic of chemical equilibrium. To satisfy these conditions it is necessary and sufficient that

$$\left. \begin{aligned} \mu_1 + g h &= \text{Const.} \\ \cdot &\cdot \\ \mu_n + g h &= \text{Const.} \end{aligned} \right\} \quad (234)$$

The expressions  $\mu_1, \dots \mu_n$  denote quantities which we have called the potentials for the several components, and which are entirely determined at any point in a mass by the nature and state of the mass about that point. We may avoid all confusion between these quantities and the potential of the force of gravity, if we distinguish the former, when necessary, as *intrinsic potentials*. The relations indicated by equations (234) may then be expressed as follows:

*When a fluid mass is in equilibrium under the influence of gravity, and has the same independently variable components throughout, the intrinsic potentials for the several components are constant in any given level, and diminish uniformly as the height increases, the difference of the values of the intrinsic potential for any component at two different levels, being equal to the work done by the force of gravity when a unit of matter falls from the higher to the lower level.*

The conditions expressed by equations (228), (233), (234) are necessary and sufficient for equilibrium, except with respect to the possible formation of masses which are not approximately identical in phase with any previously existing about the points where they may be formed. The possibility of such formations at any point is evidently independent of the action of gravity, and is determined entirely by the phase or phases of the matter about that point. The conditions of equilibrium in this respect have been discussed on pages 128–134.

But equations (228), (233), and (234) are not entirely independent. For with respect to any mass in which there are no surfaces of discontinuity (i. e., surfaces where adjacent elements of mass have finite differences of phase), one of these equations will be a consequence of the others. Thus by (228) and (234), we may obtain from (97), which will hold true of any continuous variations of phase, the equation

$$v dp = -g(m_1 \dots + m_n) dh; \quad (235)$$

$$\text{or} \quad dp = -g \gamma dh; \quad (236)$$

which will therefore hold true in any mass in which equations (228) and (234) are satisfied, and in which there are no surfaces of discontinuity. But the condition of equilibrium expressed by equation (233) has no exception with respect to surfaces of discontinuity; therefore in any mass in which such surfaces occur, it will be necessary for equilibrium, in addition to the relations expressed by equations (228) and (234), that there shall be no discontinuous change of pressure at these surfaces.

This superfluity in the particular conditions of equilibrium which we have found, as applied to a mass which is everywhere continuous

in phase, is due to the fact that we have made the elements of volume variable in position and size, while the matter initially contained in these elements is not supposed to be confined to them. Now, as the different components may move in different directions when the state of the system varies, it is evidently impossible to define the elements of volume so as always to include the same matter; we must, therefore, suppose the matter contained in the elements of volume to vary; and therefore it would be allowable to make these elements fixed in space. If the given mass has no surfaces of discontinuity, this would be much the simplest plan. But if there are any surfaces of discontinuity, it will be possible for the state of the given mass to vary, not only by infinitesimal changes of phase in the fixed elements of volume, but also by movements of the surfaces of discontinuity. It would therefore be necessary to add to our general condition of equilibrium terms relating to discontinuous changes in the elements of volume about these surfaces,—a necessity which is avoided if we consider these elements movable, as we can then suppose that each element remains always on the same side of the surface of discontinuity.

*Method of treating the preceding problem, in which the elements of volume are regarded as fixed.*

It may be interesting to see in detail how the particular conditions of equilibrium may be obtained if we regard the elements of volume as fixed in position and size, and consider the possibility of finite as well as infinitesimal changes of phase in each element of volume. If we use the character  $\Delta$  to denote the differences determined by such finite differences of phase, we may express the variation of the intrinsic energy of the whole mass in the form

$$\int \delta D\varepsilon + \int \Delta D\varepsilon, \quad (237)$$

in which the first integral extends over all the elements which are infinitesimally varied, and the second over all those which experience a finite variation. We may regard both integrals as extending throughout the whole mass, but their values will be zero except for the parts mentioned.

If we do not wish to limit ourselves to the consideration of masses so small that the force of gravity can be regarded as constant in direction and in intensity, we may use  $\mathcal{V}$  to denote the potential of the force of gravity, and express the variation of the part of the energy which is due to gravity in the form

$$-\int \mathcal{V} \delta Dm - \int \mathcal{V} \Delta Dm. \quad (238)$$

We shall then have, for the general condition of equilibrium,

$$f \delta D\varepsilon + f \Delta D\varepsilon - f T \delta Dm - f T \Delta Dm \geq 0; \quad (239)$$

and the equations of condition will be

$$f \delta D\eta + f \Delta D\eta = 0, \quad (240)$$

$$\left. \begin{aligned} f \delta Dm_1 + f \Delta Dm_1 &= 0, \\ \cdot &\cdot \cdot \cdot \cdot \cdot \cdot \\ f \delta Dm_n + f \Delta Dm_n &= 0. \end{aligned} \right\} \quad (241)$$

We may obtain a condition of equilibrium independent of these equations of condition, by subtracting these equations, multiplied each by an indeterminate constant, from condition (239). If we denote these indeterminate constants by  $T, M_1, \dots, M_n$ , we shall obtain after arranging the terms

$$\begin{aligned} & \int \delta D\varepsilon - T \delta Dm - T \delta D\eta - M_1 \delta Dm_1 \dots - M_n \delta Dm_n \\ & + \int \Delta D\varepsilon - T \Delta Dm - T \Delta D\eta - M_1 \Delta Dm_1 \dots - M_n \Delta Dm_n \geq 0. \end{aligned} \quad (242)$$

The variations, both infinitesimal and finite, in this condition are independent of the equations of condition (240) and (241), and are only subject to the condition that the varied values of  $D\varepsilon, D\eta, Dm_1, \dots, Dm_n$  for each element are determined by a certain change of phase. But as we do not suppose the same element to experience both a finite and an infinitesimal change of phase, we must have

$$\delta D\varepsilon - T \delta Dm - T \delta D\eta - M_1 \delta Dm_1 \dots - M_n \delta Dm_n \geq 0, \quad (243)$$

and

$$\Delta D\varepsilon - T \Delta Dm - T \Delta D\eta - M_1 \Delta Dm_1 \dots - M_n \Delta Dm_n \geq 0. \quad (244)$$

By equation (12), and in virtue of the necessary relation (222), the first of these conditions reduces\* to

$$\begin{aligned} (t - T) \delta D\eta + (\mu_1 - T - M_1) \delta Dm_1 \dots \\ + (\mu_n - T - M_n) \delta Dm_n \geq 0; \end{aligned} \quad (245)$$

for which it is necessary and sufficient that

$$t = T, \quad (246)$$

$$\left. \begin{aligned} \mu_1 - T &= M_1, \\ \cdot &\cdot \cdot \cdot \cdot \cdot \cdot \\ \mu_n - T &= M_n. \end{aligned} \right\} * \quad (247)$$

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\* The gravitation potential is here supposed to be defined in the usual way. But if it were defined so as to *decrease* when a body falls, we would have the sign + instead of - in these equations; i. e., for each component, the sum of the gravitation and intrinsic potentials would be constant throughout the whole mass.



Condition (244) may be reduced to the form

$$\Delta D\varepsilon - T\Delta D\eta - (T + M_1)\Delta Dm_1 \dots - (T + M_n)\Delta Dm_n \geq 0; \quad (248)$$

and by (246) and (247) to

$$\Delta D\varepsilon - t\Delta D\eta - \mu_1\Delta Dm_1 \dots - \mu_n\Delta Dm_n \geq 0. \quad (249)$$

If values determined subsequently to the change of phase are distinguished by accents, this condition may be written

$$D\varepsilon' - tD\eta' - \mu_1 Dm_1' \dots - \mu_n Dm_n' \\ - D\varepsilon + tD\eta + \mu_1 Dm_1 \dots + \mu_n Dm_n \geq 0, \quad (250)$$

which may be reduced by (93) to

$$D\varepsilon' - tD\eta' - \mu_1 Dm_1' \dots - \mu_n Dm_n' + pDv \geq 0. \quad (251)$$

Now if the element of volume  $Dv$  is adjacent to a surface of discontinuity, let us suppose  $D\varepsilon'$ ,  $D\eta'$ ,  $Dm_1'$ ,  $\dots$ ,  $Dm_n'$  to be determined (for the same element of volume) by the phase existing on the other side of the surface of discontinuity. As  $t$ ,  $\mu_1$ ,  $\dots$ ,  $\mu_n$  have the same values on both sides of this surface, the condition may be reduced by (93) to

$$-p'Dv + pDv \geq 0. \quad (252)$$

That is, the pressure must not be greater on one side of a surface of discontinuity than on the other.

Applied more generally, (251) expresses the condition of equilibrium with respect to the possibility of discontinuous changes of phases at any point. As  $Dv' = Dv$ , the condition may also be written

$$D\varepsilon' - tD\eta' + pDv' - \mu_1 Dm_1' \dots - \mu_n Dm_n' \geq 0, \quad (253)$$

which must hold true when  $t$ ,  $p$ ,  $\mu_1$ ,  $\dots$ ,  $\mu_n$  have values determined by any point in the mass, and  $D\varepsilon'$ ,  $D\eta'$ ,  $Dv'$ ,  $Dm_1'$ ,  $\dots$ ,  $Dm_n'$  have values determined by any possible phase of the substances of which the mass is composed. The application of the condition is, however, subject to the limitations considered on pages 128-134. It may easily be shown (see pages 160, 161) that for constant values of  $t$ ,  $\mu_1$ ,  $\dots$ ,  $\mu_n$ , and of  $Dv'$ , the first member of (253) will have the least possible value when  $D\varepsilon'$ ,  $D\eta'$ ,  $Dm_1'$ ,  $\dots$ ,  $Dm_n'$  are determined by a phase for which the temperature has the value  $t$ , and the potentials the values  $\mu_1$ ,  $\dots$ ,  $\mu_n$ . It will be sufficient, therefore, to consider the condition as applied to such phases, in which case it may be reduced by (93) to

$$p - p' \geq 0. \quad (254)$$

That is, the pressure at any point must be as great as that of any phase of the same components, for which the temperature and the

potentials have the same values as at that point. We may also express this condition by saying that the pressure must be as great as is consistent with equations (246), (247). This condition with the equations mentioned will always be sufficient for equilibrium; when the condition is not satisfied, if equilibrium subsists, it will be at least practically unstable.

Hence, the phase at any point of a fluid mass, which is in stable equilibrium under the influence of gravity (whether this force is due to external bodies or to the mass itself), and which has throughout the same independently variable components, is completely determined by the phase at any other point and the difference of the values of the gravitation potential for the two points.

#### FUNDAMENTAL EQUATIONS OF IDEAL GASES AND GAS-MIXTURES.

For a constant quantity of a perfect or ideal gas, the product of the volume and pressure is proportional to the temperature, and the variations of energy are proportional to the variations of temperature. For a unit of such a gas we may write

$$p v = a t,$$

$$d\varepsilon = c dt,$$

$a$  and  $c$  denoting constants. By integration, we obtain the equation

$$\varepsilon = c t + E,$$

in which  $E$  also denotes a constant. If by these equations we eliminate  $t$  and  $p$  from (11), we obtain

$$d\varepsilon = \frac{\varepsilon - E}{c} d\eta - \frac{a}{v} \frac{\varepsilon - E}{c} dv,$$

or

$$c \frac{d\varepsilon}{\varepsilon - E} = d\eta - a \frac{dv}{v}.$$

The integral of this equation may be written in the form

$$c \log \frac{\varepsilon - E}{c} = \eta - a \log v - H,$$

where  $H$  denotes a fourth constant. We may regard  $E$  as denoting the energy of a unit of the gas for  $t=0$ ;  $H$  its entropy for  $t=1$  and  $v=1$ ;  $a$  its pressure in the latter state, or its volume for  $t=1$  and  $p=1$ ;  $c$  its specific heat at constant volume. We may extend the application of the equation to any quantity of the gas, without altering the values of the constants, if we substitute  $\frac{\varepsilon}{m}$ ,  $\frac{\eta}{m}$ ,  $\frac{v}{m}$  for  $\varepsilon$ ,  $\eta$ ,  $v$ , respectively. This will give

$$c \log \frac{\varepsilon - Em}{cm} = \frac{\eta}{m} - H + a \log \frac{m}{v}. \quad (255)$$

This is a fundamental equation (see pages 140–144) for an ideal gas of invariable composition. It will be observed that if we do not have to consider the properties of the matter which forms the gas as appearing in any other form or combination, but solely as constituting the gas in question (in a state of purity), we may without loss of generality give to  $E$  and  $H$  the value zero, or any other arbitrary values. But when the scope of our investigations is not thus limited, we may have determined the states of the substance of the gas for which  $\varepsilon=0$  and  $\eta=0$  with reference to some other form in which the substance appears, or, if the substance is compound, the states of its components for which  $\varepsilon=0$  and  $\eta=0$  may be already determined; so that the constants  $E$  and  $H$  cannot in general be treated as arbitrary.

We obtain from (255) by differentiation

$$\frac{c}{\varepsilon - Em} d\varepsilon = \frac{1}{m} d\eta - \frac{a}{v} dv + \left( \frac{cE}{\varepsilon - Em} + \frac{c+a}{m} - \frac{\eta}{m^2} \right) dm, \quad (256)$$

whence, in virtue of the general relation expressed by (86),

$$t = \frac{\varepsilon - Em}{cm}, \quad (257)$$

$$p = a \frac{\varepsilon - Em}{cv}, \quad (258)$$

$$\mu = E + \frac{\varepsilon - Em}{cm^2} (cm + am - \eta). \quad (259)$$

We may obtain the fundamental equation between  $\psi$ ,  $t$ ,  $v$ , and  $m$  from equations (87), (255), and (257). Eliminating  $\varepsilon$  we have

$$\psi = Em + cmt - t\eta,$$

and 
$$c \log t = \frac{\eta}{m} - H + a \log \frac{m}{v};$$

and eliminating  $\eta$ , we have the fundamental equation

$$\psi = Em + mt \left( c - H - c \log t + a \log \frac{m}{v} \right). \quad (260)$$

Differentiating this equation, we obtain

$$\begin{aligned} d\psi = & -m \left( H + c \log t + a \log \frac{v}{m} \right) dt - \frac{amt}{v} dv \\ & + \left( E + t \left( c + a - H - c \log t + a \log \frac{m}{v} \right) \right) dm; \end{aligned} \quad (261)$$

whence, by the general equation (88),

$$\eta = m \left( H + c \log t + a \log \frac{v}{m} \right), \quad (262)$$

$$p = \frac{a m t}{v}, \quad (263)$$

$$\mu = E + t \left( c + a - H - c \log t + a \log \frac{m}{v} \right). \quad (264)$$

From (260), by (87) and (91), we obtain

$$\zeta = Em + m t \left( c - H - c \log t + a \log \frac{m}{v} \right) + p v,$$

and eliminating  $v$  by means of (263), we obtain the fundamental equation

$$\zeta = Em + m t \left( c + a - H - (c + a) \log t + a \log \frac{p}{a} \right). \quad (265)$$

From this, by differentiation and comparison with (92), we may obtain the equations

$$\eta = m \left( H + (c + a) \log t - a \log \frac{p}{a} \right), \quad (266)$$

$$v = \frac{a m t}{p}, \quad (267)$$

$$\mu = E + t \left( c + a - H - (c + a) \log t + a \log \frac{p}{a} \right). \quad (268)$$

The last is also a fundamental equation. It may be written in the form

$$\log \frac{p}{a} = \frac{H - c - a}{a} + \frac{c + a}{a} \log t + \frac{\mu - E}{a t}, \quad (269)$$

or, if we denote by  $e$  the base of the Napierian system of logarithms,

$$p = a e^{\frac{H - c - a}{a}} t^{\frac{c + a}{a}} e^{\frac{\mu - E}{a t}} \quad (270)$$

The fundamental equation between  $\chi$ ,  $\eta$ ,  $p$ , and  $m$  may also be easily obtained; it is

$$(c + a) \log \frac{\chi - Em}{(c + a)m} = \frac{\eta}{m} - H + a \log \frac{p}{a}, \quad (271)$$

which can be solved with respect to  $\chi$ .

Any one of the fundamental equations (255), (260), (265), (270), and (271), which are entirely equivalent to one another, may be



regarded as defining an ideal gas. It will be observed that most of these equations might be abbreviated by the use of different constants. In (270), for example, a single constant might be used for

$\alpha e^{\frac{H-c-a}{a}}$ , and another for  $\frac{c+a}{a}$ . The equations have been given

in the above form, in order that the relations between the constants occurring in the different equations might be most clearly exhibited. The sum  $c+a$  is the specific heat for constant pressure, as appears if we differentiate (266) regarding  $p$  and  $m$  as constant.\*

\* We may easily obtain the equation between the temperature and pressure of a saturated vapor, if we know the fundamental equations of the substance both in the gaseous, and in the liquid or solid state. If we suppose that the density and the specific heat at constant pressure of the liquid may be regarded as constant quantities (for such moderate pressures as the liquid experiences while in contact with the vapor), and denote this specific heat by  $k$ , and the volume of a unit of the liquid by  $V$ , we shall have for a unit of the liquid

$$t \, d\eta = k \, dt,$$

whence

$$\eta = k \log t + H',$$

where  $H'$  denotes a constant. Also, from this equation and (97),

$$d\mu = -(k \log t + H') \, dt + V \, dp,$$

whence

$$\mu = kt - kt \log t - H' t + Vp + E', \quad (A)$$

where  $E'$  denotes another constant. This is a fundamental equation for the substance in the liquid state. If (268) represents the fundamental equation for the same substance in the gaseous state, the two equations will both hold true of coexistent liquid and gas. Eliminating  $\mu$  we obtain

$$\log \frac{p}{a} = \frac{H-H'+k-c-a}{a} - \frac{k-c-a}{a} \log t - \frac{E-E'}{at} + \frac{V}{a} \frac{p}{t}.$$

If we neglect the last term, which is evidently equal to the density of the vapor divided by the density of the liquid, we may write

$$\log p = A - B \log t - \frac{C}{t},$$

$A$ ,  $B$ , and  $C$  denoting constants. If we make similar suppositions in regard to the substance in the solid state, the equation between the pressure and temperature of coexistent solid and gaseous phases will of course have the same form.

A similar equation will also apply to the phases of an ideal gas which are coexistent with two different kinds of solids, one of which can be formed by the combination of the gas with the other, each being of invariable composition and of constant specific heat and density. In this case we may write for one solid

$$\mu_1 = k't - k't \log t - H't + V'p + E',$$

and for the other

$$\mu_2 = k''t - k''t \log t - H''t + V''p + E'',$$

and for the gas

$$\mu_3 = E + t \left( c + a - H - (c+a) \log t + a \log \frac{p}{a} \right).$$

The preceding fundamental equations all apply to gases of *constant composition*, for which the matter is entirely determined by a single

Now if a unit of the gas unites with the quantity  $\lambda$  of the first solid to form the quantity  $1 + \lambda$  of the second it will be necessary for equilibrium (see pages 121, 122) that

$$\mu_3 + \lambda \mu_1 = (1 + \lambda) \mu_2.$$

Substituting the values of  $\mu_1, \mu_2, \mu_3$ , given above, we obtain after arranging the terms and dividing by  $at$

$$\log \frac{p}{a} = A - B \log t - \frac{C}{t} + D \frac{p}{t},$$

when

$$A = \frac{H + \lambda H' - (1 + \lambda) H'' - c - a - \lambda k' + (1 + \lambda) k''}{a},$$

$$B = \frac{(1 + \lambda) k'' - \lambda k' - c - a}{a},$$

$$C = \frac{E + \lambda E' - (1 + \lambda) E''}{a}, \quad D = \frac{(1 + \lambda) V'' - \lambda V'}{a}.$$

We may conclude from this that an equation of the same form may be applied to an ideal gas in equilibrium with a liquid of which it forms an independently variable component, when the specific heat and density of the liquid are entirely determined by its composition, except that the letters  $A, B, C$ , and  $D$  must in this case be understood to denote quantities which vary with the composition of the liquid. But to consider the case more in detail, we have for the liquid by (A)

$$\frac{\zeta}{m} = \mu = kt - kt \log t - H't + Vp + E',$$

where  $k, H', V, E'$  denote quantities which depend only upon the composition of the liquid. Hence, we may write

$$\zeta = \mathbf{k}t - \mathbf{k}t \log t - \mathbf{H}t + \mathbf{V}p + \mathbf{E},$$

where  $\mathbf{k}, \mathbf{H}, \mathbf{V}$ , and  $\mathbf{E}$  denote functions of  $m_1, m_2$ , etc. (the quantities of the several components of the liquid). Hence, by (92),

$$\mu_1 = \frac{d\mathbf{k}}{dm_1} t - \frac{d\mathbf{k}}{dm_1} t \log t - \frac{d\mathbf{H}}{dm_1} t + \frac{d\mathbf{V}}{dm_1} p + \frac{d\mathbf{E}}{dm_1}.$$

If the component to which this potential relates is that which also forms the gas, we shall have by (269)

$$\log \frac{p}{a} = \frac{H - c - a}{a} + \frac{c + a}{a} \log t + \frac{\mu_1 - E}{at}.$$

Eliminating  $\mu_1$ , we obtain the equation

$$\log \frac{p}{a} = A - B \log t - \frac{C}{t} + D \frac{p}{t},$$

in which  $A, B, C$ , and  $D$  denote quantities which depend only upon the composition of the liquid, viz:

$$A = \frac{1}{a} \left( H - \frac{d\mathbf{H}}{dm_1} - c - a + \frac{d\mathbf{k}}{dm_1} \right),$$

$$B = \frac{1}{a} \left( \frac{d\mathbf{k}}{dm_1} - c - a \right),$$

variable ( $m$ ). We may obtain corresponding fundamental equations for a mixture of gases, in which the proportion of the components shall be variable, from the following considerations.

It is a rule which admits of a very general and in many cases very exact experimental verification, that if several liquid or solid substances which yield different gases or vapors are simultaneously in equilibrium with a mixture of these gases (cases of chemical action between the gases being excluded,) the pressure in the gas-mixture is equal to the sum of the pressures of the gases yielded at the same temperature by the various liquid or solid substances taken separately. Now the potential in any of the liquids or solids for the substance which it yields in the form of gas has very nearly the same value when the liquid or solid is in equilibrium with the gas-mixture as when it is in equilibrium with its own gas alone. The difference of the pressure in the two cases will cause a certain difference in the values of the potential, but that this difference will be small, we may infer from the equation

$$\left(\frac{d\mu_1}{dp}\right)_{t, m} = \left(\frac{dv}{dm_1}\right)_{t, p, m}, \quad (272)$$

which may be derived from equation (92). In most cases, there will be a certain absorption by each liquid of the gases yielded by the others, but as it is well known that the above rule does not apply to cases in which such absorption takes place to any great extent, we may conclude that the effect of this circumstance in the cases with which we have to do is of secondary importance. If we neglect the slight differences in the values of the potentials due to these circumstances, the rule may be expressed as follows:

*The pressure in a mixture of different gases is equal to the sum of the pressures of the different gases as existing each by itself at the same temperature and with the same value of its potential.*

To form a precise idea of the practical significance of the law as thus stated with reference to the equilibrium of two liquids with a mixture of the gases which they emit, when neither liquid absorbs the gas emitted by the other, we may imagine a long tube closed at each end and bent in the form of a W to contain in each of the descending

$$C = \frac{1}{a} \left( E - \frac{d\mathbf{E}}{dm_1} \right) \quad D = \frac{1}{a} \frac{d\mathbf{V}}{dm_1}.$$

With respect to some of the equations which have here been deduced, the reader may compare Professor Kirchhoff "Ueber die Spannung des Dampfes von Mischungen aus Wasser und Schwefelsäure," Pogg. Ann., vol. civ. (1858), p. 612; and Dr. Rankine "On Saturated Vapors," Phil. Mag., vol. xxxi. (1866), p. 199.

loops one of the liquids, and above these liquids the gases which they emit, viz., the separate gases at the ends of the tube, and the mixed gases in the middle. We may suppose the whole to be in equilibrium, the difference of the pressures of the gases being balanced by the proper heights of the liquid columns. Now it is evident from the principles established on pages 203–210 that the potential for either gas will have the same value in the mixed and in the separate gas *at the same level*, and therefore according to the rule in the form which we have given, the pressure in the gas-mixture is equal to the sum of the pressures in the separate gases, *all these pressures being measured at the same level*. Now the experiments by which the rule has been established relate rather to the gases in the vicinity of the surfaces of the liquids. Yet, although the differences of level in these surfaces may be considerable, the corresponding differences of pressure in the columns of gas will certainly be very small in all cases which can be regarded as falling under the laws of ideal gases, for which very great pressures are not admitted.

If we apply the above law to a mixture of ideal gases and distinguish by subscript numerals the quantities relating to the different gases, and denote by  $\Sigma_1$  the sum of all similar terms obtained by changing the subscript numerals, we shall have by (270)

$$p = \Sigma_1 \left( a_1 e^{\frac{H_1 - c_1 - a_1}{a_1}} t^{\frac{c_1 + a_1}{a_1}} e^{\frac{\mu_1 - E_1}{a_1 t}} \right), \quad (273)$$

It will be legitimate to assume this equation provisionally as the fundamental equation defining an ideal gas-mixture, and afterwards to justify the suitableness of such a definition by the properties which may be deduced from it. In particular, it will be necessary to show that an ideal gas-mixture as thus defined, when the proportion of its components remains constant, has all the properties which have already been assumed for an ideal gas of invariable composition; it will also be desirable to consider more rigorously and more in detail the equilibrium of such a gas-mixture with solids and liquids, with respect to the above rule.

By differentiation and comparison with (98) we obtain

$$\frac{\eta}{v} = \Sigma_1 \left( (c_1 + a_1 - \frac{\mu_1 - E_1}{t}) e^{\frac{H_1 - c_1 - a_1}{a_1}} t^{\frac{c_1 + a_1}{a_1}} e^{\frac{\mu_1 - E_1}{a_1 t}} \right), \quad (274)$$



$$\left. \begin{aligned} \frac{m_1}{v} &= e^{\frac{H_1 - c_1 - a_1}{a_1}} t^{\frac{c_1}{a_1}} e^{\frac{\mu_1 - E_1}{a_1 t}}, \\ \frac{m_2}{v} &= e^{\frac{H_2 - c_2 - a_2}{a_2}} t^{\frac{c_2}{a_2}} e^{\frac{\mu_2 - E_2}{a_2 t}}, \\ \text{etc.} \end{aligned} \right\} \quad (275)$$

Equations (275) indicate that the relation between the temperature, the density of any component, and the potential for that component, is not affected by the presence of the other components. They may also be written

$$\mu_1 = E_1 + t \left( c_1 + a_1 - H_1 - c_1 \log t + a_1 \log \frac{m_1}{v} \right), \quad \left\{ \begin{array}{l} (276) \\ \text{etc.} \end{array} \right.$$

Eliminating  $\mu_1, \mu_2$ , etc. from (273) and (274) by means of (275) and (276), we obtain

$$p = \sum_1 \frac{a_1 m_1 t}{v}, \quad (277)$$

$$\eta = \sum_1 \left( m_1 H_1 + m_1 c_1 \log t + m_1 a_1 \log \frac{v}{m_1} \right). \quad (278)$$

Equation (277) expresses the familiar principle that the pressure in a gas-mixture is equal to the sum of the pressures which the component gases would possess if existing separately with the same volume at the same temperature. Equation (278) expresses a similar principle in regard to the entropy of the gas-mixture.

From (276) and (277) we may easily obtain the fundamental equation between  $\psi, t, v, m_1, m_2$ , etc. For by substituting in (94) the values of  $p, \mu_1, \mu_2$ , etc. taken from these equations, we obtain

$$\psi = \sum_1 \left( E_1 m_1 + m_1 t \left( c_1 - H_1 - c_1 \log t + a_1 \log \frac{m_1}{v} \right) \right). \quad (279)$$

If we regard the proportion of the various components as constant, this equation may be simplified by writing

$$\begin{aligned} m &\text{ for } \sum_1 m_1, \\ c m &\text{ for } \sum_1 (c_1 m_1), \\ a m &\text{ for } \sum_1 (a_1 m_1), \\ E m &\text{ for } \sum_1 (E_1 m_1), \end{aligned}$$

and  $H m - a m \log m$  for  $\sum_1 (H_1 m_1 - a_1 m_1 \log m_1)$ .

The values of  $c, a, E$ , and  $H$ , will then be constant and  $m$  will denote the total quantity of gas. As the equation will thus be reduced to the

form of (260), it is evident that an ideal gas-mixture, as defined by (273) or (279), when the proportion of its components remains unchanged, will have all the properties which we have assumed for an ideal gas of invariable composition. The relations between the specific heats of the gas-mixture at constant volume and at constant pressure and the specific heats of its components are expressed by the equations

$$c = \sum_1 \frac{m_1 c_1}{m}, \quad (280)$$

and

$$c + a = \sum_1 \frac{m_1 (c_1 + a_1)}{m}. \quad (281)$$

We have already seen that the values of  $t$ ,  $v$ ,  $m_1$ ,  $\mu_1$  in a gas-mixture are such as are possible for the component  $G_1$  (to which  $m_1$  and  $\mu_1$  relate) existing separately. If we denote by  $p_1$ ,  $\eta_1$ ,  $\psi_1$ ,  $\varepsilon_1$ ,  $\chi_1$ ,  $\zeta_1$  the connected values of the several quantities which the letters indicate determined for the gas  $G_1$  as thus existing separately, and extend this notation to the other components, we shall have by (273), (274), and (279)

$$p = \sum_1 p_1, \quad \eta = \sum_1 \eta_1, \quad \psi = \sum_1 \psi_1; \quad (282)$$

whence by (87), (89), and (91)

$$\varepsilon = \sum_1 \varepsilon_1, \quad \chi = \sum_1 \chi_1, \quad \zeta = \sum_1 \zeta_1. \quad (283)$$

The quantities  $p$ ,  $\eta$ ,  $\psi$ ,  $\varepsilon$ ,  $\chi$ ,  $\zeta$  relating to the gas-mixture may therefore be regarded as consisting of parts which may be attributed to the several components in such a manner that between the parts of these quantities which are assigned to any component, the quantity of that component, the potential for that component, the temperature, and the volume, the same relations shall subsist as if that component existed separately. It is in this sense that we should understand the law of Dalton, that every gas is as a vacuum to every other gas.

It is to be remarked that these relations are consistent and possible for a mixture of gases which are not ideal gases, and indeed without any limitation in regard to the thermodynamic properties of the individual gases. They are all consequences of the law that the pressure in a mixture of different gases is equal to the sum of the pressures of the different gases as existing each by itself at the same temperature and with the same value of its potential. For let  $p_1$ ,  $\eta_1$ ,  $\varepsilon_1$ ,  $\psi_1$ ,  $\chi_1$ ,  $\zeta_1$ ;  $p_2$ , etc.; etc. be defined as relating to the different gases existing each by itself with the same volume, temperature, and potential as in the gas-mixture; if

$$p = \sum_1 p_1,$$

then 
$$\left(\frac{dp}{d\mu_1}\right)_{t, \mu_2 \dots \mu_n} = \left(\frac{dp_1}{d\mu_1}\right)_t;$$

and therefore, by (98), the quantity of any component gas  $G_1$  in the gas-mixture, and in the separate gas to which  $p_1$ ,  $\eta_1$ , etc. relate, is the same and may be denoted by the same symbol  $m_1$ . Also

$$\eta = v \left(\frac{dp}{dt}\right)_{\mu_1, \dots \mu_n} = v \sum_1 \left(\frac{dp}{dt}\right)_{\mu_1} = \sum_1 \eta_1;$$

whence also, by (93)–(96),

$$\varepsilon = \sum_1 \varepsilon_1, \quad \psi = \sum_1 \psi_1, \quad \chi = \sum_1 \chi_1, \quad \zeta = \sum_1 \zeta_1.$$

All the same relations will also hold true whenever the value of  $\psi$  for the gas-mixture is equal to the sum of the values of this function for the several component gases existing each by itself in the same quantity as in the gas-mixture and with the temperature and volume of the gas-mixture. For if  $p_1$ ,  $\eta_1$ ,  $\varepsilon_1$ ,  $\psi_1$ ,  $\chi_1$ ,  $\zeta_1$ ;  $p_2$ , etc.; etc. are defined as relating to the components existing thus by themselves, we shall have

$$\psi = \sum_1 \psi_1,$$

whence

$$\left(\frac{d\psi}{dm_1}\right)_{t, v, m} = \left(\frac{d\psi_1}{dm_1}\right)_{t, v}.*$$

Therefore, by (88), the potential  $\mu_1$  has the same value in the gas-mixture and in the gas  $G_1$  existing separately as supposed. Moreover,

$$\eta = - \left(\frac{d\psi}{dt}\right)_{v, m} = - \sum_1 \left(\frac{d\psi_1}{dt}\right)_{v, m} = \sum_1 \eta_1,$$

and 
$$p = - \left(\frac{d\psi}{dv}\right)_{t, m} = - \sum_1 \left(\frac{d\psi_1}{dv}\right)_{t, m} = \sum_1 p_1,$$

whence

$$\varepsilon = \sum_1 \varepsilon_1, \quad \chi = \sum_1 \chi_1, \quad \zeta = \sum_1 \zeta_1.$$

Whenever different bodies are combined without communication of work or heat between them and external bodies, the energy of the body formed by the combination is necessarily equal to the sum of the energies of the bodies combined. In the case of ideal gas-mixtures, when the initial temperatures of the gas-masses which are combined

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\* A subscript  $m$  after a differential coefficient relating to a body having several independently variable components is used here and elsewhere in this paper to indicate that each of the quantities  $m_1$ ,  $m_2$ , etc., unless its differential occurs in the expression to which the suffix is applied, is to be regarded as constant in the differentiation.

are the same, (whether these gas-masses are entirely different gases, or gas-mixtures differing only in the proportion of their components,) the condition just mentioned can only be satisfied when the temperature of the resultant gas-mixture is also the same. In such combinations, therefore, the final temperature will be the same as the initial.

If we consider a vertical column of an ideal gas-mixture which is in equilibrium, and denote the densities of one of its components at two different points by  $\gamma_1$  and  $\gamma_1'$ , we shall have by (275) and (234)

$$\frac{\gamma_1}{\gamma_1'} = e^{\frac{\mu_1 - \mu_1'}{a_1 t}} = e^{\frac{g(h' - h)}{a_1 t}}. \quad (284)$$

From this equation, in which we may regard the quantities distinguished by accents as constant, it appears that the relation between the density of any one of the components and the height is not affected by the presence of the other components.

The work obtained or expended in any reversible process of combination or separation of ideal gas-mixtures at constant temperature, or when the temperatures of the initial and final gas-masses and of the only external source of heat or cold which is used are all the same, will be found by taking the difference of the sums of the values of  $\psi$  for the initial, and for the final gas-masses. (See pages 145, 146). It is evident from the form of equation (279) that this work is equal to the sum of the quantities of work which would be obtained or expended in producing in each different component existing separately the same changes of density which that component experiences in the actual process for which the work is sought.\*

We will now return to the consideration of the equilibrium of a liquid with the gas which it emits as affected by the presence of different gases, when the gaseous mass in contact with the liquid may be regarded as an ideal gas-mixture.

It may first be observed, that the density of the gas which is emitted by the liquid will not be affected by the presence of other gases which are not absorbed by the liquid, when the liquid is protected in any way from the pressure due to these additional gases. This may be accomplished by separating the liquid and gaseous

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\* This result has been given by Lord Rayleigh, (Phil. Mag., vol. xlix, 1875, p. 311). It will be observed that equation (279) might be deduced immediately from this principle in connection with equation (260) which expresses the properties ordinarily assumed for perfect gases.



masses by a diaphragm which is permeable to the liquid. It will then be easy to maintain the liquid at any constant pressure which is not greater than that in the gas. The potential in the liquid for the substance which it yields as gas will then remain constant, and therefore the potential for the same substance in the gas and the density of this substance in the gas and the part of the gaseous pressure due to it will not be affected by the other components of the gas.

But when the gas and liquid meet under ordinary circumstances, i. e., in a free plane surface, the pressure in both is necessarily the same, as also the value of the potential for any common component  $S_1$ . Let us suppose the density of an insoluble component of the gas to vary, while the composition of the liquid and the temperature remain unchanged. If we denote the increments of pressure and of the potential for  $S_1$  by  $dp$  and  $d\mu_1$ , we shall have by (272)

$$d\mu_1 = \left( \frac{d\mu_1}{dp} \right)_{t, m}^{(L)} dp = \left( \frac{dv}{dm_1} \right)_{t, p, m}^{(L)} dp,$$

the index (L) denoting that the expressions to which it is affixed refer to the liquid. (Expressions without such an index will refer to the gas alone or to the gas and liquid in common.) Again, since the gas is an ideal gas-mixture, the relation between  $p_1$  and  $\mu_1$  is the same as if the component  $S_1$  existed by itself at the same temperature, and therefore by (268)

$$d\mu_1 = a_1 t d \log p_1.$$

Therefore

$$a_1 t d \log p_1 = \left( \frac{dv}{dm_1} \right)_{t, p, m}^{(L)} dp. \quad (285)$$

This may be integrated at once if we regard the differential coefficient in the second member as constant, which will be a very close approximation. We may obtain a result more simple, but not quite so accurate, if we write the equation in the form

$$dp_1 = \gamma_1 \left( \frac{dv}{dm_1} \right)_{t, p, m}^{(L)} dp, \quad (286)$$

where  $\gamma_1$  denotes the density of the component  $S_1$  in the gas, and integrate regarding this quantity also as constant. This will give

$$p_1 - p_1' = \gamma_1 \left( \frac{dv}{dm_1} \right)_{t, p, m}^{(L)} (p - p'). \quad (287)$$

where  $p_1'$  and  $p'$  denote the values of  $p_1$  and  $p$  when the insoluble component of the gas is entirely wanting. It will be observed that  $p - p'$  is nearly equal to the pressure of the insoluble component, in the phase of the gas-mixture to which  $p_1$  relates.  $S_1$  is not neces-

sarily the only common component of the gas and liquid. If there are others, we may find the increase of the part of the pressure in the gas-mixture belonging to any one of them by equations differing from the last only in the subscript numerals.

Let us next consider the effect of a gas which is absorbed to some extent, and which must therefore in strictness be regarded as a component of the liquid. We may commence by considering in general the equilibrium of a gas-mixture of two components  $S_1$  and  $S_2$  with a liquid formed of the same components. Using a notation like the previous, we shall have by (98) for constant temperature,

$$dp = \gamma_1 d\mu_1 + \gamma_2 d\mu_2,$$

and

$$dp = \gamma_1^{(L)} d\mu_1 + \gamma_2^{(L)} d\mu_2;$$

whence

$$(\gamma_1^{(L)} - \gamma_1) d\mu_1 = (\gamma_2 - \gamma_2^{(L)}) d\mu_2.$$

Now if the gas is an ideal gas-mixture,

$$d\mu_1 = \frac{a_1 t}{p_1} dp_1 = \frac{dp_1}{\gamma_1}, \quad \text{and} \quad d\mu_2 = \frac{a_2 t}{p_2} dp_2 = \frac{dp_2}{\gamma_2},$$

therefore

$$\left( \frac{\gamma_1^{(L)}}{\gamma_1} - 1 \right) dp_1 = \left( 1 - \frac{\gamma_2^{(L)}}{\gamma_2} \right) dp_2. \quad (288)$$

We may now suppose that  $S_1$  is the principal component of the liquid, and  $S_2$  is a gas which is absorbed in the liquid to a slight extent. In such cases it is well known that the ratio of the densities of the substance  $S_2$  in the liquid and in the gas is for a given temperature approximately constant. If we denote this constant by  $A$ , we shall have

$$\left( \frac{\gamma_1^{(L)}}{\gamma_1} - 1 \right) dp_1 = (1 - A) dp_2. \quad (289)$$

It would be easy to integrate this equation regarding  $\gamma_1$  as variable, but as the variation in the value of  $p_1$  is necessarily very small we shall obtain sufficient accuracy if we regard  $\gamma_1$  as well as  $\gamma_1^{(L)}$  as constant. We shall thus obtain

$$\left( \frac{\gamma_1^{(L)}}{\gamma_1} - 1 \right) (p_1 - p_1') = (1 - A) p_2, \quad (290)$$

where  $p_1'$  denotes the pressure of the saturated vapor of the pure liquid consisting of  $S_1$ . It will be observed that when  $A = 1$ , the presence of the gas  $S_2$  will not affect the pressure or density of the gas  $S_1$ . When  $A < 1$ , the pressure and density of the gas  $S_1$  are greater than if  $S_2$  were absent, and when  $A > 1$ , the reverse is true.

The properties of an ideal gas-mixture (according to the definition which we have assumed) when in equilibrium with liquids or solids have been developed at length, because it is only in respect to these properties that there is any variation from the properties usually attributed to perfect gases. As the pressure of a gas saturated with vapor is usually given as a little less than the sum of the pressure of the gas calculated from its density and that of saturated vapor in a space otherwise empty, while our formulæ would make it a little more, when the gas is insoluble, it would appear that in this respect our formulæ are less accurate than the rule which would make the pressure of the gas saturated with vapor equal to the sum of the two pressures mentioned. Yet the reader will observe that the magnitude of the quantities concerned is not such that any stress can be laid upon this circumstance.

It will also be observed that the statement of Dalton's law which we have adopted, while it serves to complete the theory of gas-mixtures (with respect to a certain class of properties), asserts nothing with reference to any solid or liquid bodies. But the common rule that the density of a gas necessary for equilibrium with a solid or liquid is not altered by the presence of a different gas which is not absorbed by the solid or liquid, if construed *strictly*, will involve consequences in regard to solids and liquids which are entirely inadmissible. To show this, we will assume the correctness of the rule mentioned. Let  $S_1$  denote the common component of the gaseous and liquid or solid masses, and  $S_2$  the insoluble gas, and let quantities relating to the gaseous mass be distinguished when necessary by the index (G), and those relating to the liquid or solid by the index (L). Now while the gas is in equilibrium with the liquid or solid, let the quantity which it contains of  $S_2$  receive the increment  $dm_2$ , its volume and the quantity which it contains of the other component, as well as the temperature, remaining constant. The potential for  $S_1$  in the gaseous mass will receive the increment

$$\left(\frac{d\mu_1}{dm_2}\right)_{t, v, m}^{(G)} dm_2$$

and the pressure will receive the increment

$$\left(\frac{dp}{dm_2}\right)_{t, v, m}^{(G)} dm_2.$$

Now the liquid or solid remaining in equilibrium with the gas must experience the same variations in the values of  $\mu_1$  and  $p$ . But by (272)

$$\left(\frac{d\mu_1}{dp}\right)_{t, m}^{(L)} = \left(\frac{dv}{dm_1}\right)_{t, p, m}^{(L)}.$$

Therefore,

$$\left(\frac{dv}{dm_1}\right)_{t, p, m}^{(L)} = \frac{\left(\frac{d\mu_1}{dm_2}\right)_{t, v, m}^{(G)}}{\left(\frac{dp}{dm_2}\right)_{t, v, m}^{(G)}}.$$

It will be observed that the first member of this equation relates solely to the liquid or solid, and the second member solely to the gas. Now we may suppose the same gaseous mass to be capable of equilibrium with several different liquids or solids, and the first member of this equation must therefore have the same value for all such liquids or solids; which is quite inadmissible. In the simplest case, in which the liquid or solid is identical in substance with the vapor which it yields, it is evident that the expression in question denotes the reciprocal of the density of the solid or liquid. Hence, when a gas is in equilibrium with one of its components both in the solid and liquid states (as when a moist gas is in equilibrium with ice and water), it would be necessary that the solid and liquid should have the same density.

The foregoing considerations appear sufficient to justify the definition of an ideal gas-mixture which we have chosen. It is of course immaterial whether we regard the definition as expressed by equation (273), or by (279), or by any other fundamental equation which can be derived from these.

The fundamental equations for an ideal gas-mixture corresponding to (255), (265), and (271) may easily be derived from these equations by using inversely the substitutions given on page 217. They are

$$\sum_1 (c_1 m_1) \log \frac{\varepsilon - \sum_1 (E_1 m_1)}{\sum_1 (c_1 m_1)} = \eta + \sum_1 (a_1 m_1 \log \frac{m_1}{v} - H_1 m_1), \quad (291)$$

$$\begin{aligned} \sum_1 (c_1 m_1 + a_1 m_1) \log \frac{\chi - \sum_1 (E_1 m_1)}{\sum_1 (c_1 m_1 + a_1 m_1)} \\ = \eta + \sum_1 \left( a_1 m_1 \log \frac{p m_1}{\sum_1 (a_1 m_1)} - H_1 m_1 \right), \end{aligned} \quad (292)$$

$$\begin{aligned} \zeta = \sum_1 \left( E_1 m_1 + m_1 t (c_1 + a_1 - H_1) \right) \\ - \sum_1 (c_1 m_1 + a_1 m_1) t \log t + \sum_1 \left( a_1 m_1 t \log \frac{p m_1}{\sum_1 (a_1 m_1)} \right). \end{aligned} \quad (293)$$

The components to which the fundamental equations (273), (279), (291), (292), 293) refer, may themselves be gas-mixtures. We may for example apply the fundamental equations of a binary gas-mixture



to a mixture of hydrogen and air, or to any ternary gas-mixture in which the proportion of two of the components is fixed. In fact, the form of equation (279) which applies to a gas-mixture of any particular number of components may easily be reduced, when the proportions of some of these components are fixed, to the form which applies to a gas-mixture of a smaller number of components. The necessary substitutions will be analogous to those given on page 217. But the components must be entirely different from one another with respect to the gases of which they are formed by mixture. We cannot, for example, apply equation (279) to a gas-mixture in which the components are oxygen and air. It would indeed be easy to form a fundamental equation for such a gas-mixture with reference to the designated gases as components. Such an equation might be derived from (279) by the proper substitutions. But the result would be an equation of more complexity than (279). A *chemical* compound, however, with respect to Dalton's law, and with respect to all the equations which have been given, is to be regarded as entirely different from its components. Thus, a mixture of hydrogen, oxygen, and vapor of water is to be regarded as a ternary gas-mixture, having the three components mentioned. This is certainly true when the quantities of the compound gas and of its components are all independently variable in the gas-mixture, without change of temperature or pressure. Cases in which these quantities are not thus independently variable will be considered hereafter.

*Inferences in regard to Potentials in Liquids and Solids.*

Such equations as (264), (268), (276), by which the values of potentials in pure or mixed gases may be derived from quantities capable of direct measurement, have an interest which is not confined to the theory of gases. For as the potentials of the independently variable components which are common to coexistent liquid and gaseous masses have the same values in each, these expressions will generally afford the means of determining for liquids, at least approximately, the potential for any independently variable component which is capable of existing in the gaseous state. For although every state of a liquid is not such as can exist in contact with a gaseous mass, it will always be possible, when any of the components of the liquid are volatile, to bring it by a change of pressure alone, its temperature and composition remaining unchanged, to a state for which there is a coexistent phase of vapor, in which

the values of the potentials of the volatile components of the liquid may be estimated from the density of these substances in the vapor. The variations of the potentials in the liquid due to the change of pressure will in general be quite trifling as compared with the variations which are connected with changes of temperature or of composition, and may moreover be readily estimated by means of equation (272). The same considerations will apply to volatile solids with respect to the determination of the potential for the substance of the solid.

As an application of this method of determining the potentials in liquids, let us make use of the law of Henry in regard to the absorption of gases by liquids to determine the relation between the quantity of the gas contained in any liquid mass and its potential. Let us consider the liquid as in equilibrium with the gas, and let  $m_1^{(G)}$  denote the quantity of the gas existing as such,  $m_1^{(L)}$  the quantity of the same substance contained in the liquid mass,  $\mu_1$  the potential for this substance common to the gas and liquid,  $v^{(G)}$  and  $v^{(L)}$  the volumes of the gas and liquid. When the absorbed gas forms but a very small part of the liquid mass, we have by Henry's law

$$\frac{m_1^{(L)}}{v^{(L)}} = A \frac{m_1^{(G)}}{v^{(G)}}, \quad (294)$$

where  $A$  is a function of the temperature; and by (276)

$$\mu_1 = B + C \log \frac{m_1^{(G)}}{v^{(G)}}, \quad (295)$$

$B$  and  $C$  also denoting functions of the temperature. Therefore

$$\mu_1 = B + C \log \frac{m_1^{(L)}}{A v^{(L)}}. \quad (296)$$

It will be seen (if we disregard the difference of notation) that this equation is equivalent in form to (216), which was deduced from *a priori* considerations as a probable relation between the quantity and the potential of a small component. When a liquid absorbs several gases at once, there will be several equations of the form of (296), which will hold true simultaneously, and which we may regard as equivalent to equations (217), (218). The quantities  $A$  and  $C$  in (216), with the corresponding quantities in (217), (218), were regarded as functions of the temperature and pressure, but since the potentials in liquids are but little affected by the pressure, we might anticipate that these quantities in the case of liquids might be regarded as functions of the temperature alone.

In regard to equations (216), (217), (218), we may now observe that by (264) and (276) they are shown to hold true in ideal gases or gas-mixtures, not only for components which form only a small part of the whole gas-mixture, but without any such limitation, and not only approximately but absolutely. It is noticeable that in this case quantities  $A$  and  $C$  are functions of the temperature alone, and do not even depend upon the nature of the gaseous mass, except upon the particular component to which they relate. As all gaseous bodies are generally supposed to approximate to the laws of ideal gases when sufficiently rarefied, we may regard these equations as approximately valid for gaseous bodies in general when the density is sufficiently small. When the density of the gaseous mass is very great, but the separate density of the component in question is small, the equations will probably hold true, but the values of  $A$  and  $C$  may not be entirely independent of the pressure, or of the composition of the mass in respect to its principal components. These equations will also apply, as we have just seen, to the potentials in liquid bodies for components of which the density in the liquid is very small, whenever these components exist also in the gaseous state, and conform to the law of Henry. This seems to indicate that the law expressed by these equations has a very general application.

*Considerations relating to the Increase of Entropy due to the Mixture of Gases by Diffusion.*

From equation (278) we may easily calculate the increase of entropy which takes place when two different gases are mixed by diffusion, at a constant temperature and pressure. Let us suppose that the quantities of the gases are such that each occupies initially one half of the total volume. If we denote this volume by  $V$ , the increase of entropy will be

$$m_1 a_1 \log V + m_2 a_2 \log V - m_1 a_1 \log \frac{V}{2} - m_2 a_2 \log \frac{V}{2},$$

or  $(m_1 a_1 + m_2 a_2) \log 2.$

Now  $m_1 a_1 = \frac{pV}{2t},$  and  $m_2 a_2 = \frac{pV}{2t}.$

Therefore the increase of entropy may be represented by the expression

$$\frac{pV}{t} \log 2. \quad (297)$$

It is noticeable that the value of this expression does not depend upon the kinds of gas which are concerned, if the quantities are such as has been supposed, except that the gases which are mixed must be

of different kinds. If we should bring into contact two masses of the same kind of gas, they would also mix, but there would be no increase of entropy. But in regard to the relation which this case bears to the preceding, we must bear in mind the following considerations. When we say that when two different gases mix by diffusion, as we have supposed, the energy of the whole remains constant, and the entropy receives a certain increase, we mean that the gases could be separated and brought to the same volume and temperature which they had at first by means of certain changes in external bodies, for example, by the passage of a certain amount of heat from a warmer to a colder body. But when we say that when two gas-masses of the same kind are mixed under similar circumstances there is no change of energy or entropy, we do not mean that the gases which have been mixed can be separated without change to external bodies. On the contrary, the separation of the gases is entirely impossible. We call the energy and entropy of the gas-masses when mixed the same as when they were unmixed, because we do not recognize any difference in the substance of the two masses. So when gases of different kinds are mixed, if we ask what changes in external bodies are necessary to bring the system to its original state, we do not mean a state in which each particle shall occupy more or less exactly the same position as at some previous epoch, but only a state which shall be undistinguishable from the previous one in its sensible properties. It is to states of systems thus incompletely defined that the problems of thermodynamics relate.

But if such considerations explain why the mixture of gas-masses of the same kind stands on a different footing from the mixture of gas-masses of different kinds, the fact is not less significant that the increase of entropy due to the mixture of gases of different kinds, in such a case as we have supposed, is independent of the nature of the gases.

Now we may without violence to the general laws of gases which are embodied in our equations suppose other gases to exist than such as actually do exist, and there does not appear to be any limit to the resemblance which there might be between two such kinds of gas. But the increase of entropy due to the mixing of given volumes of the gases at a given temperature and pressure would be independent of the degree of similarity or dissimilarity between them. We might also imagine the case of two gases which should be absolutely identical in all the properties (sensible and molecular) which come into play while they exist as gases either pure or mixed with each other,



but which should differ in respect to the attractions between their atoms and the atoms of some other substances, and therefore in their tendency to combine with such substances. In the mixture of such gases by diffusion an increase of entropy would take place, although the process of mixture, dynamically considered, might be absolutely identical in its minutest details (even with respect to the precise path of each atom) with processes which might take place without any increase of entropy. In such respects, entropy stands strongly contrasted with energy. Again, when such gases have been mixed, there is no more impossibility of the separation of the two kinds of molecules in virtue of their ordinary motions in the gaseous mass without any especial external influence, than there is of the separation of a homogeneous gas into the same two parts into which it has once been divided, after these have once been mixed. In other words, the impossibility of an uncompensated decrease of entropy seems to be reduced to improbability.

There is perhaps no fact in the molecular theory of gases so well established as that the number of molecules in a given volume at a given temperature and pressure is the same for every kind of gas when in a state to which the laws of ideal gases apply. Hence the quantity  $\frac{pV}{t}$  in (297) must be entirely determined by the number of molecules which are mixed. And the increase of entropy is therefore determined by the number of these molecules and is independent of their dynamical condition and of the degree of difference between them.

The result is of the same nature when the volumes of the gases which are mixed are not equal, and when more than two kinds of gas are mixed. If we denote by  $v_1, v_2$ , etc., the initial volumes of the different kinds of gas, and by  $V$  as before the total volume, the increase of entropy may be written in the form

$$\sum_1 (m_1 a_1) \log V - \sum_1 (m_1 a_1 \log v_1).$$

And if we denote by  $r_1, r_2$ , etc., the numbers of the molecules of the several different kinds of gas, we shall have

$$r_1 = C m_1 a_1, \quad r_2 = C m_2 a_2, \quad \text{etc.},$$

where  $C$  denotes a constant. Hence

$$v_1 : V :: m_1 a_1 : \sum_1 (m_1 a_1) :: r_1 : \sum_1 r_1;$$

and the increase of entropy may be written

$$\frac{\sum_1 r_1 \log \sum_1 r_1 - \sum_1 (r_1 \log r_1)}{C}. \quad (298)$$

*The Phases of Dissipated Energy of an Ideal Gas-mixture with Components which are Chemically Related.*

We will now pass to the consideration of the phases of dissipated energy (see page 200) of an ideal gas-mixture, in which the number of the proximate components exceeds that of the ultimate.

Let us first suppose that an ideal gas-mixture has for proximate components the gases  $G_1$ ,  $G_2$ , and  $G_3$ , the units of which are denoted by  $\mathfrak{G}_1$ ,  $\mathfrak{G}_2$ ,  $\mathfrak{G}_3$ , and that in ultimate analysis

$$\mathfrak{G}_3 = \lambda_1 \mathfrak{G}_1 + \lambda_2 \mathfrak{G}_2, \quad (299)$$

$\lambda_1$  and  $\lambda_2$  denoting positive constants, such that  $\lambda_1 + \lambda_2 = 1$ . The phases which we are to consider are those for which the energy of the gas-mixture is a minimum for constant entropy and volume and constant quantities of  $G_1$  and  $G_2$ , as determined in ultimate analysis. For such phases, by (86),

$$\mu_1 \delta m_1 + \mu_2 \delta m_2 + \mu_3 \delta m_3 \geq 0. \quad (300)$$

for such values of the variations as do not affect the quantities of  $G_1$  and  $G_2$  as determined in ultimate analysis. Values of  $\delta m_1$ ,  $\delta m_2$ ,  $\delta m_3$  proportional to  $\lambda_1$ ,  $\lambda_2$ ,  $-1$ , and only such, are evidently consistent with this restriction: therefore

$$\lambda_1 \mu_1 + \lambda_2 \mu_2 = \mu_3. \quad (301)$$

If we substitute in this equation values of  $\mu_1$ ,  $\mu_2$ ,  $\mu_3$  taken from (276), we obtain, after arranging the terms and dividing by  $t$ ,

$$\lambda_1 a_1 \log \frac{m_1}{v} + \lambda_2 a_2 \log \frac{m_2}{v} - a_3 \log \frac{m_3}{v} = A + B \log t - \frac{C}{t}, \quad (302)$$

where

$$A = \lambda_1 H_1 + \lambda_2 H_2 - H_3 - \lambda_1 c_1 - \lambda_2 c_2 + c_3 - \lambda_1 a_1 - \lambda_2 a_2 + a_3, \quad (303)$$

$$B = \lambda_1 c_1 + \lambda_2 c_2 - c_3, \quad (304)$$

$$C = \lambda_1 E_1 + \lambda_2 E_2 - E_3. \quad (305)$$

If we denote by  $\beta_1$  and  $\beta_2$  the volumes (determined under standard conditions of temperature and pressure) of the quantities of the gases  $G_1$  and  $G_2$  which are contained in a unit of volume of the gas  $G_3$ , we shall have

$$\beta_1 = \frac{\lambda_1 a_1}{a_3}, \text{ and } \beta_2 = \frac{\lambda_2 a_2}{a_3}, \quad (306)$$

and (302) will reduce to the form

$$\log \frac{m_1^{\beta_1} m_2^{\beta_2}}{m_3 v^{\beta_1 + \beta_2 - 1}} = \frac{A}{a_3} + \frac{B}{a_3} \log t - \frac{C}{a_3 t}. \quad (307)$$

Moreover, as by (277)

$$p v = (a_1 m_1 + a_2 m_2 + a_3 m_3) t, \quad (308)$$

we have on eliminating  $v$

$$\log \frac{m_1^{\beta_1} m_2^{\beta_2} p^{\beta_1 + \beta_2 - 1}}{m_3 (a_1 m_1 + a_2 m_2 + a_3 m_3)^{\beta_1 + \beta_2 - 1}} = \frac{A}{a_3} + \frac{B'}{a_3} \log t - \frac{C}{a_3 t}, \quad (309)$$

where

$$B' = \lambda_1 c_1 + \lambda_2 c_2 - c_3 + \lambda_1 a_1 + \lambda_2 a_2 - a_3. \quad (310)$$

It will be observed that the quantities  $\beta_1, \beta_2$  will always be positive and have a simple relation to unity, and that the value of  $\beta_1 + \beta_2 - 1$  will be positive or zero, according as gas  $G_3$  is formed of  $G_1$  and  $G_2$  with or without condensation. If we should assume, according to the rule often given for the specific heat of compound gases, that the thermal capacity at constant volume of any quantity of the gas  $G_3$  is equal to the sum of the thermal capacities of the quantities which it contains of the gases  $G_1$  and  $G_2$ , the value of  $B$  would be zero. The heat evolved in the formation of a unit of the gas  $G_3$  out of the gases  $G_1$  and  $G_2$ , without mechanical action, is by (283) and (257)

$$\lambda_1 (c_1 t + E_1) + \lambda_2 (c_2 t + E_2) - (c_3 t + E_3),$$

or

$$Bt + C,$$

which will reduce to  $C$  when the above relation in regard to the specific heats is satisfied. In any case the quantity of heat thus evolved divided by  $a_3 t^2$  will be equal to the differential coefficient of the second member of equation (307) with respect to  $t$ . Moreover, the heat evolved in the formation of a unit of the gas  $G_3$  out of the gases  $G_1$  and  $G_2$  under constant pressure is

$$Bt + C + \lambda_1 a_1 t + \lambda_2 a_2 t - a_3 t = B't + C,$$

which is equal to the differential coefficient of the second member of (309) with respect to  $t$ , multiplied by  $a_3 t^2$ .

It appears by (307) that, except in the case when  $\beta_1 + \beta_2 = 1$ , for any given finite values of  $m_1, m_2, m_3$ , and  $t$  (infinitesimal values being excluded as well as infinite), it will always be possible to assign such a finite value to  $v$  that the mixture shall be in a state of dissipated energy. Thus, if we regard a mixture of hydrogen, oxygen, and vapor of water as an ideal gas-mixture, for a mixture containing any given quantities of these three gases at any given tem-

perature there will be a certain volume at which the mixture will be in a state of dissipated energy. In such a state no such phenomenon as explosion will be possible, and no formation of water by the action of platinum. (If the mass should be expanded beyond this volume, the only possible action of a catalytic agent would be to resolve the water into its components.) It may indeed be true that at ordinary temperatures, except when the quantity either of hydrogen or of oxygen is very small compared with the quantity of water, the state of dissipated energy is one of such extreme rarefaction as to lie entirely beyond our power of experimental verification. It is also to be noticed that a state of great rarefaction is so unfavorable to any condensation of the gases, that it is quite probable that the catalytic action of platinum may cease entirely at a degree of rarefaction far short of what is necessary for a state of dissipated energy. But with respect to the theoretical demonstration, such states of great rarefaction are precisely those to which we should suppose that the laws of ideal gas-mixtures would apply most perfectly.

But when the compound gas  $G_3$  is formed of  $G_1$  and  $G_2$  without condensation, (i. e., when  $\beta_1 + \beta_2 = 1$ .) it appears from equation (307) that the relation between  $m_1$ ,  $m_2$ , and  $m_3$  which is necessary for a phase of dissipated energy is determined by the temperature alone.

In any case, if we regard the total quantities of the gases  $G_1$  and  $G_2$  (as determined by the ultimate analysis of the gas-mixture), and also the volume, as constant, the quantities of these gases which appear uncombined in a phase of dissipated energy will increase with the temperature, if the formation of the compound  $G_3$  *without change of volume* is attended with evolution of heat. Also, if we regard the total quantities of the gases  $G_1$  and  $G_2$ , and also the pressure, as constant, the quantities of these gases which appear uncombined in a phase of dissipated energy, will increase with the temperature, if the formation of the compound  $G_3$  *under constant pressure* is attended with evolution of heat. If  $B = 0$ , (a case, as has been seen, of especial importance), the heat obtained by the formation of a unit of  $G_3$  out of  $G_1$  and  $G_2$  without change of volume or of temperature will be equal to  $C$ . If this quantity is positive, and the total quantities of the gases  $G_1$  and  $G_2$  and also the volume have given finite values, for an infinitesimal value of  $t$  we shall have (for a phase of dissipated energy) an infinitesimal value either of  $m_1$  or of  $m_2$ , and for an infinite value of  $t$  we shall have finite (neither infinitesimal nor infinite) values of  $m_1$ ,  $m_2$ , and  $m_3$ . But if we suppose the pressure instead of the volume to have a given finite value (with



suppositions otherwise the same), we shall have for infinitesimal values of  $t$  an infinitesimal value either of  $m_1$  or  $m_2$ , and for infinite values of  $t$  finite or infinitesimal values of  $m_3$  according as  $\beta_1 + \beta_2$  is equal to or greater than unity.

The case which we have considered is that of a ternary gas-mixture, but our results may easily be generalized in this respect. In fact, whatever the number of component gases in a gas-mixture, if there are relations of equivalence in ultimate analysis between these components, such relations may be expressed by one or more equations of the form

$$\lambda_1 \mathfrak{G}_1 + \lambda_2 \mathfrak{G}_2 + \lambda_3 \mathfrak{G}_3 + \text{etc.} = 0, \quad (311)$$

where  $\mathfrak{G}_1, \mathfrak{G}_2$ , etc. denote the units of the various component gases, and  $\lambda_1, \lambda_2$ , etc. denote positive or negative constants such that  $\sum_1 \lambda_1 = 0$ . From (311) with (86) we may derive for phases of dissipated energy,

$$\lambda_1 \mu_1 + \lambda_2 \mu_2 + \lambda_3 \mu_3 + \text{etc.} = 0,$$

$$\text{or} \quad \sum_1 (\lambda_1 \mu_1) = 0. \quad (312)$$

Hence, by (276),

$$\sum_1 \left( \lambda_1 a_1 \log \frac{m_1}{v} \right) = A + B \log t - \frac{C}{t}, \quad (313)$$

where  $A, B$  and  $C$  are constants determined by the equations

$$A = \sum_1 (\lambda_1 H_1 - \lambda_1 c_1 - \lambda_1 a_1), \quad (314)$$

$$B = \sum_1 (\lambda_1 c_1), \quad (315)$$

$$C = \sum_1 (\lambda_1 E_1). \quad (316)$$

Also, since  $p v = \sum_1 (a_1 m_1) t$ ,

$$\begin{aligned} \sum_1 (\lambda_1 a_1 \log m_1) - \sum (\lambda_1 a_1) \log \sum_1 (a_1 m_1) \\ + \sum (\lambda_1 a_1) \log p = A + B' \log t - \frac{C}{t}, \end{aligned} \quad (317)$$

where

$$B' = \sum_1 (\lambda_1 c_1 + \lambda_1 a_1). \quad (318)$$

If there is more than one equation of the form (311), we shall have more than one of each of the forms (313) and (317), which will hold true simultaneously for phases of dissipated energy.

It will be observed that the relations necessary for a phase of dissipated energy between the volume and temperature of an ideal gas-mixture, and the quantities of the components which take part in the chemical processes, and the pressure due to these components, are not affected by the presence of neutral gases in the gas-mixture.

From equations (312) and (234) it follows that if there is a phase of dissipated energy at any point in an ideal gas-mixture in equilibrium under the influence of gravity, the whole gas-mixture must consist of such phases.

The equations of the phases of dissipated energy of a binary gas-mixture, the components of which are identical in substance, are comparatively simple in form. In this case the two components have the same potential, and if we write  $\beta$  for  $\frac{a_1}{a_2}$  (the ratio of the volumes of equal quantities of the two components under the same conditions of temperature and pressure), we shall have

$$\log \frac{m_1^\beta}{m_2 v^{\beta-1}} = \frac{A}{a_2} + \frac{B}{a_2} \log t - \frac{C}{a_2 t}, \quad (319)$$

$$\log \frac{m_1^\beta p^{\beta-1}}{m_2 (a_1 m_1 + a_2 m_2)^{\beta-1}} = \frac{A}{a_2} + \frac{B'}{a_2} \log t - \frac{C}{a_2 t}; \quad (320)$$

where

$$A = H_1 - H_2 - c_1 + c_2 - a_1 + a_2, \quad (321)$$

$$B = c_1 - c_2, \quad B' = c_1 - c_2 + a_1 - a_2, \quad (322)$$

$$C = E_1 - E_2. \quad (323)$$

#### *Gas-mixtures with Convertible Components.*

The equations of the phases of dissipated energy of ideal gas-mixtures which have components of which some are identical in ultimate analysis to others have an especial interest in relation to the theory of gas-mixtures in which the components are not only thus equivalent, but are actually transformed into each other within the gas-mixture on variations of temperature and pressure, so that quantities of these (proximate) components are entirely determined, at least in any permanent phase of the gas-mixture, by the quantities of a smaller number of ultimate components, with the temperature and pressure. Such gas-mixtures may be distinguished as having *convertible components*. The very general considerations adduced on pages 197–203, which are not limited in their application to gaseous bodies, suggest the hypothesis that the equations of the phases of dissipated energy of ideal gas-mixtures may apply to such gas-mixtures as have been described. It will, however, be desirable to consider the matter more in detail.

In the first place, if we consider the case of a gas-mixture which only differs from an ordinary ideal gas-mixture for which some of the components are equivalent in that there is perfect freedom in regard to the transformation of these components, it follows at once from the general formula of equilibrium (1) or (2) that equilibrium is only possible for such phases as we have called phases of dissipated energy, for which some of the characteristic equations have been deduced in the preceding pages.

If it should be urged, that regarding a gas-mixture which has convertible components as an ideal gas-mixture of which, for some reason, only a part of the phases are actually capable of existing, we might still suppose the particular phases which alone can exist to be determined by some other principle than that of the free convertibility of the components (as if, perhaps, the case were analogous to one of *constraint* in mechanics), it may easily be shown that such a hypothesis is entirely untenable, when the quantities of the proximate components may be varied independently by suitable variations of the temperature and pressure, and of the quantities of the ultimate components, and it is admitted that the relations between the energy, entropy, volume, temperature, pressure, and the quantities of the several proximate components in the gas-mixture are the same as for an ordinary ideal gas-mixture, in which the components are not convertible. Let us denote the quantities of the  $n'$  proximate components of a gas-mixture  $A$  by  $m_1, m_2$ , etc., and the quantities of its  $n$  ultimate components by  $\mathbf{m}_1, \mathbf{m}_2$ , etc. ( $n$  denoting a number less than  $n'$ ), and let us suppose that for this gas-mixture the quantities  $\varepsilon, \eta, v, t, p, m_1, m_2$ , etc. satisfy the relations characteristic of an ideal gas-mixture, while the phase of the gas-mixture is entirely determined by the values of  $\mathbf{m}_1, \mathbf{m}_2$ , etc., with two of the quantities  $\varepsilon, \eta, v, t, p$ . We may evidently imagine such an ideal gas-mixture  $B$  having  $n'$  components (not convertible), that every phase of  $A$  shall correspond with one of  $B$  in the values of  $\varepsilon, \eta, v, t, p, m_1, m_2$ , etc. Now let us give to the quantities  $\mathbf{m}_1, \mathbf{m}_2$ , etc. in the gas-mixture  $A$  any fixed values, and for the body thus defined let us imagine the  $v\text{-}\eta\text{-}\varepsilon$  surface (see page 174) constructed; likewise for the ideal gas-mixture  $B$  let us imagine the  $v\text{-}\eta\text{-}\varepsilon$  surface constructed for every set of values of  $m_1, m_2$ , etc. which is consistent with the given values of  $\mathbf{m}_1, \mathbf{m}_2$ , etc., i. e., for every body of which the *ultimate* composition would be expressed by the given values of  $\mathbf{m}_1, \mathbf{m}_2$ , etc. It follows immediately from our supposition, that every point in the  $v\text{-}\eta\text{-}\varepsilon$  surface relating to  $A$  must coincide with some point of one of the  $v\text{-}\eta\text{-}\varepsilon$  surfaces relating

to  $B$  not only in respect to position but also in respect to its tangent plane (which represents temperature and pressure); therefore the  $v$ - $\eta$ - $\varepsilon$  surface relating to  $A$  must be tangent to the various  $v$ - $\eta$ - $\varepsilon$  surfaces relating to  $B$ , and therefore must be an envelop of these surfaces. From this it follows that the points which represent phases common to both gas-mixtures must represent the phases of dissipated energy of the gas-mixture  $B$ .

The properties of an ideal gas-mixture which are assumed in regard to the gas-mixture of convertible components in the above demonstration are expressed by equations (277) and (278) with the equation

$$\varepsilon = \sum_1 (c_1 m_1 t + m_1 E_1). \quad (324)$$

It is usual to assume in regard to gas-mixtures having convertible components that the convertibility of the components does not affect the relations (277) and (324). The same cannot be said of the equation (278). But in a very important class of cases it will be sufficient if the applicability of (277) and (324) is admitted. The cases referred to are those in which in certain phases of a gas-mixture the components are convertible, and in other phases of the same proximate composition the components are not convertible, and the equations of an ideal gas-mixture hold true.

If there is only a single degree of convertibility between the components, (i. e., if only a single kind of conversion, with its reverse, can take place among the components,) it will be sufficient to assume, in regard to the phases in which conversion takes place, the validity of equation (277) and of the following, which can be derived from (324) by differentiation, and comparison with equation (11), which expresses a necessary relation,

$$[t d\eta - p dv - \sum_1 (c_1 m_1) dt]_m = 0.* \quad (325)$$

We shall confine our demonstration to this case. It will be observed that the physical signification of (325) is that if the gas-mixture is subjected to such changes of volume and temperature as do not alter its proximate composition, the heat absorbed or yielded may be calculated by the same formula as if the components were not convertible.

Let us suppose the thermodynamic state of a gaseous mass  $M$ , of such a kind as has just been described, to be varied while within the limits within which the components are not convertible. (The quantities of the proximate components, therefore, as well as of the ulti-

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\* This notation is intended to indicate that  $m_1$ ,  $m_2$ , etc. are regarded as constant



mate, are supposed constant). If we use the same method of geometrical representation as before, the point representing the volume, entropy, and energy of the mass will describe a line in the  $v$ - $\eta$ - $\epsilon$  surface of an ideal gas-mixture of inconvertible components, the form and position of this surface being determined by the proximate composition of  $M$ . Let us now suppose the same mass to be carried beyond the limit of inconvertibility, the variations of state after passing the limit being such as not to alter its proximate composition. It is evident that this will in general be possible. Exceptions can only occur when the limit is formed by phases in which the proximate composition is uniform. The line traced in the region of convertibility must belong to the same  $v$ - $\eta$ - $\epsilon$  surface of an ideal gas-mixture of inconvertible components as before, continued beyond the limit of inconvertibility for the components of  $M$ , since the variations of volume, entropy and energy are the same as would be possible if the components were not convertible. But it must also belong to the  $v$ - $\eta$ - $\epsilon$  surface of the body  $M$ , which is here a gas-mixture of convertible components. Moreover, as the inclination of each of these surfaces must indicate the temperature and pressure of the phases through which the body passes, these two surfaces must be tangent to each other along the line which has been traced. As the  $v$ - $\eta$ - $\epsilon$  surface of the body  $M$  in the region of convertibility must thus be tangent to all the surfaces representing ideal gas-mixtures of every possible proximate composition consistent with the ultimate composition of  $M$ , continued beyond the region of inconvertibility, in which alone their form and position may be capable of experimental demonstration, the former surface must be an envelop of the latter surfaces, and therefore a continuation of the surface of the phases of dissipated energy in the region of inconvertibility.

The foregoing considerations may give a measure of *a priori* probability to the results which are obtained by applying the ordinary laws of ideal gas-mixtures to cases in which the components are convertible. It is only by experiments upon gases in phases in which their components are convertible that the validity of any of these results can be established.

The very accurate determinations of density which have been made for the peroxide of nitrogen enable us to subject some of our equations to a very critical test. That this substance in the gaseous state is properly regarded as a mixture of different gases can hardly be doubted, as the proportion of the components derived from its density on the supposition that one component has the molecular formula

$\text{NO}_2$  and the other the formula  $\text{N}_2\text{O}_4$  is the same as that derived from the depth of the color on the supposition that the absorption of light is due to one of the components alone, and is proportioned to the separate density of that component.\*

MM. Sainte-Claire Deville and Troost† have given a series of determinations of what we shall call the *relative densities* of peroxide of nitrogen at various temperatures under atmospheric pressure. We use the term *relative density* to denote what it is usual in treatises on chemistry to denote by the term *density*, viz., the actual density of a gas divided by the density of a standard perfect gas at the same pressure and temperature, the standard gas being air, or more strictly, an ideal gas which has the same density as air at the zero of the centigrade scale and the pressure of one atmosphere. In order to test our equations by these determinations, it will be convenient to transform equation (320), so as to give directly the relation between the relative density, the pressure, and the temperature.

As the density of the standard gas at any given temperature and pressure may by (263) be expressed by the formula  $\frac{p}{a_s t}$ , the relative density of a binary gas-mixture may be expressed by

$$D = (m_1 + m_2) \frac{a_s t}{p v}. \quad (326)$$

Now by (263)

$$a_1 m_1 + a_2 m_2 = \frac{p v}{t}. \quad (327)$$

By giving to  $m_2$  and  $m_1$  successively the value zero in these equations, we obtain

$$D_1 = \frac{a_s}{a_1}, \quad D_2 = \frac{a_s}{a_2}, \quad (328)$$

where  $D_1$  and  $D_2$  denote the values of  $D$  when the gas consists wholly of one or of the other component. If we assume that

$$D_2 = 2 D_1, \quad (329)$$

we shall have

$$a_1 = 2 a_2. \quad (330)$$

From (326) we have

$$m_1 + m_2 = D \frac{p v}{a_s t},$$

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\* Salet, "Sur la coloration du peroxyde d'azote," *Comptes Rendus*, vol. lxvii, p. 488.

† *Comptes Rendus*, vol. lxiv, p. 237.

and from (327), by (328) and (330),

$$2 m_1 + m_2 = D_2 \frac{p v}{a_s t} = 2 D_1 \frac{p v}{a_s t},$$

whence

$$m_1 = (D_2 - D) \frac{p v}{a_s t} \quad (331)$$

$$m_2 = 2 (D - D_1) \frac{p v}{a_s t} \quad (332)$$

By (327), (331), and (332) we obtain from (320)

$$\log \frac{(D_2 - D)^2 p}{2 (D - D_1) a_s} = \frac{A}{a_2} + \frac{B'}{a_2} \log t - \frac{C}{t}. \quad (333)$$

This formula will be more convenient for purposes of calculation if we introduce common logarithms (denoted by  $\log_{10}$ ) instead of hyperbolic, the temperature of the ordinary contigra<sup>d</sup> scale  $t_c$  instead of the absolute temperature  $t$ , and the pressure in atmospheres  $p_{at}$  instead of  $p$  the pressure in a rational system of units. If we also add the logarithm of  $a_s$  to both sides of the equation, we obtain

$$\log_{10} \frac{(D_2 - D)^2 p_{at}}{2 (D - D_1)} = \mathbf{A} + \frac{B'}{a_2} \log_{10} (t_c + 273) - \frac{\mathbf{C}}{t_c + 273}, \quad (334)$$

where  $\mathbf{A}$  and  $\mathbf{C}$  denote constants, the values of which are closely connected with those of  $A$  and  $C$ .

From the molecular formulæ of peroxide of nitrogen  $\text{NO}_2$  and  $\text{N}_2\text{O}_4$ , we may calculate the relative densities

$$D_1 = \frac{14 + 32}{2} .0691 = 1.589, \text{ and } D_2 = \frac{28 + 64}{2} .0691 = 3.178. \quad (335)$$

The determinations of MM. Deville and Troost are satisfactorily represented by the equation

$$\log_{10} \frac{(3.178 - D)^2 p_{at}}{2 (D - 1.589)} = 9.47056 - \frac{3118.6}{t_c + 273}, \quad (336)$$

which gives

$$D = 3.178 + \Theta - \sqrt{\Theta (3.178 + \Theta)}$$

$$\text{where } \log_{10} \Theta = 9.47056 - \frac{3118.6}{t_c + 273} - \log_{10} p_{at}.$$

In the first part of the following table are given in successive columns the temperature and pressure of the gas in the several experiments of MM. Deville and Troost, the relative densities calculated from these numbers by equation (336), the relative densities as observed, and the difference of the observed and calculated relative

densities. It will be observed that these differences are quite small, in no case reaching .03, and on the average scarcely exceeding .01. The significance of such correspondence in favor of the hypothesis by means of which equation (336) has been established is of course diminished by the fact that two constants in the equation have been determined from these experiments. If the same equation can be shown to give correctly the relative densities at other pressures than that for which the constants have been determined, such correspondence will be much more decisive.

$t_c$	$p_{at}$	$D$ calculated by eq. (336).	$D$ observed.	diff.	Observers.
26.7	1	2.676	2.65	— .026	D. & T.
35.4	1	2.524	2.53	+ .006	D. & T.
39.8	1	2.443	2.46	+ .017	D. & T.
49.6	1	2.256	2.27	+ .014	D. & T.
60.2	1	2.067	2.08	+ .013	D. & T.
70.0	1	1.920	1.92	.000	D. & T.
80.6	1	1.801	1.80	— .001	D. & T.
90.0	1	1.728	1.72	— .008	D. & T.
100.1	1	1.676	1.68	+ .004	D. & T.
111.3	1	1.641	1.65	+ .009	D. & T.
121.5	1	1.622	1.62	— .002	D. & T.
135.0	1	1.607	1.60	— .007	D. & T.
154.0	1	1.597	1.58	— .017	D. & T.
183.2	1	1.592	1.57	— .022	D. & T.
97.5	1	1.687			
97.5	$\frac{10450}{26397}$	1.631	1.783	+ .152	P. & W.
24.5	1	2.711			
24.5	$\frac{18090}{42629}$	2.524	2.52	— .004	P. & W.
11.3	1	2.891			
11.3	$\frac{9265}{44245}$	2.620	2.645	+ .025	P. & W.
4.2	1	2.964			
4.2	$\frac{6023}{35438}$	2.708	2.588	— .120	P. & W.

Messrs. Playfair and Wanklyn have published\* four determinations of the relative density of peroxide of nitrogen at various temperatures when diluted with nitrogen. Since the relations expressed by equations (319) and (320) are not affected by the presence of a third gas which is different from the gases  $G_1$  and  $G_2$  (to which  $m_1$  and  $m_2$  relate) and neutral to them, (see the remark at the foot of page 233),—provided that we take  $p$  to denote the pressure which we attribute to the gases  $G_1$  and  $G_2$ , i. e., the total pressure diminished by the pressure which the third gas would exert if occupying alone the same space at the same temperature,—it follows that the relations expressed for

\*Transactions of the Royal Society of Edinburgh, vol. xxii, p. 441.



peroxide of nitrogen by (333), (334), and (336) will not be affected by the presence of free nitrogen, if the pressure expressed by  $p$  or  $p_{at}$  and contained implicitly in the symbol  $D$  (see equation (326) by which  $D$  is defined) is understood to denote the total pressure diminished by the pressure due to the free nitrogen. The determinations of Playfair and Wanklyn are given in the latter part of the above table. The pressures given are those obtained by subtracting the pressure due to the free nitrogen from the total pressure. We may suppose such reduced pressures to have been used in the reduction of the observations by which the numbers in the column of observed relative densities were obtained. Besides the relative densities calculated by equation (336) for the temperatures and (reduced) pressures of the observations, the table contains the relative densities calculated for the same temperatures and the pressure of one atmosphere.

The reader will observe that in the second and third experiments of Playfair and Wanklyn there is a very close accordance between the calculated and observed values of  $D$ , while in the second and fourth experiments there is a considerable difference. Now the weight to be attributed to the several determinations is very different. The quantities of peroxide of nitrogen which were used in the several experiments were respectively .2410, .5893, .3166, and .2016 grammes. For a rough approximation, we may assume that the probable errors of the relative densities are inversely proportional to these numbers. This would make the probable error of the first and fourth observations two or three times as great as that of the second and considerably greater than that of the third. We must also observe that in the first of these experiments, the observed relative density 1.783 is greater than 1.687, the relative density calculated by equation (336) for the temperature of the experiment and the pressure of one atmosphere. Now the number 1.687 we may regard as established directly by the experiments of Deville and Troost. For in seven successive experiments in this part of the series the calculated relative densities differ from the observed by less than .01. If then we accept the numbers given by experiment, the effect of diluting the gas with nitrogen is to increase its relative density. As this result is entirely at variance with the facts observed in the case of other gases, and in the case of this gas at lower temperatures, as appears from the three other determinations of Playfair and Wanklyn, it cannot possibly be admitted on the strength of a single

observation. The first experiment of this series cannot therefore properly be used as a test of our equations. Similar considerations apply with somewhat less force to the last experiment. By comparing the temperatures and pressures of the three last experiments with the observed relative densities, the reader may easily convince himself that if we admit the substantial accuracy of the determinations in the two first of these experiments (the second and third of the series, which have the greatest weight), the last determination of relative density 2.588 must be too small. In fact, it should evidently be greater than the number in the preceding experiment 2.645.

If we confine our attention to the second and third experiments of the series, the agreement is as good as could be desired. Nor will the admission of errors of .152 and .120 (certainly not large in determinations of this kind) in the first and fourth experiments involve any serious doubt of the substantial accuracy of the second and third, when the difference of weight of the determinations is considered. Yet it is much to be desired that the relation expressed by (336), or with more generality by (334), should be tested by more numerous experiments.

It should be stated that the numbers in the column of pressures are not quite accurate. In the experiments of Deville and Troost the gas was subject to the actual atmospheric pressure at the time of the experiment. This varied from 747 to 764 millimeters of mercury. The precise pressure for each experiment is not given. In the experiments of Playfair and Wanklyn the mixture of nitrogen and peroxide of nitrogen was subject to the actual atmospheric pressure at the time of the experiment. The numbers in the column of pressures express the fraction of the whole pressure which remains after subtracting the part due to the free nitrogen. But no indication is given in the published account of the experiments in regard to the height of the barometer. Now it may easily be shown that a variation of  $\frac{1}{760}$  in the value of  $p$  can in no case cause a variation of more than .005 in the value of  $D$  as calculated by equation (336). In any of the experiments of Playfair and Wanklyn a variation of more than 30<sup>mm</sup> in the height of the barometer would be necessary to produce a variation of .01 in the value of  $D$ . The errors due to this source cannot therefore be very serious. They might have been avoided altogether in the discussion of the experiments of Deville and Troost by using instead of (336) a formula expressing the relation between the relative density, the temperature, and the actual density, as the reciprocal of the latter quantity is given for each ex-

periment of this series. It seemed best, however, to make a trifling sacrifice of accuracy for the sake of simplicity.

It might be thought that the experiments under discussion would be better represented by a formula in which the term containing  $\log t$  (see equation (333)) was retained. But an examination of the figures in the table will show that nothing important can be gained in this respect, and there is hardly sufficient motive for adding another term to the formula of calculation. Any attempt to determine the *real* values of  $A$ ,  $B'$ , and  $C$  in equation (333), (assuming the absolute validity of such an equation for peroxide of nitrogen,) from the experiments under discussion would be entirely misleading, as the reader may easily convince himself.

From equation (336), however, the following conclusions may be deduced. By comparison with (334) we obtain

$$A + \frac{B'}{a_2} \log_{10} t - \frac{C}{t} = 9.47056 - \frac{3118.6}{t},$$

which must hold true approximately between the temperatures  $11^\circ$  and  $90^\circ$ . (At higher temperatures the relative densities vary too slowly with the temperatures to afford a critical test of the accuracy of this relation.) By differentiation we obtain

$$\frac{MB'}{a_2 t} + \frac{C}{t^2} = \frac{3118.6}{t^2},$$

where  $M$  denotes the modulus of the common system of logarithms. Now by comparing equations (333) and (334) we see that

$$C = \frac{MC}{a_2} = .43429 \frac{C}{a_2}.$$

Hence

$$B't + C = 7181 a_2 = 3590 a_1,$$

which may be regarded as a close approximation at  $40^\circ$  or  $50^\circ$ , and a tolerable approximation between the limits of temperature above mentioned. Now  $B't + C$  represents the heat evolved by the conversion of a unit of  $\text{NO}_2$  into  $\text{N}_2\text{O}_4$  under constant pressure. Such conversion cannot take place at constant pressure without change of temperature, which renders the experimental verification of the last equation less simple. But since by equations (322)

$$B' = B + a_1 - a_2 = B + \frac{1}{2} a_1,$$

we shall have for the temperature of  $40^\circ$

$$Bt + C = 3434 a_1.$$

Now  $Bt + C$  represents the decrease of energy when a unit of  $\text{NO}_2$  is transformed into  $\text{N}_2\text{O}_4$  without change of temperature. It therefore

represents the excess of the heat evolved over the work done by external forces when a mass of the gas is compressed at constant temperature until a unit of  $\text{NO}_2$  has been converted into  $\text{N}_2\text{O}_4$ . This quantity will be constant if  $B = 0$ , i. e., if the specific heats at constant volume of  $\text{NO}_2$  and  $\text{N}_2\text{O}_4$  are the same. This assumption would be more simple from a theoretical stand-point and perhaps safer than the assumption that  $B' = 0$ . If  $B = 0$ ,  $B' = a_2$ . If we wish to embody this assumption in the equation between  $D$ ,  $p$ , and  $t$ , we may substitute

$$6.5228 + \log_{10} (t_c + 273) - \frac{2977.4}{t_c + 273}$$

for the second member of equation (336). The relative densities calculated by the equation thus modified from the temperatures and pressures of the experiments under discussion will not differ from those calculated from the unmodified equation by more than .002 in any case, or by more than .001 in the first series of experiments.

It is to be noticed that if we admit the validity of the volumetrical relation expressed by equation (333), which is evidently equivalent to an equation between  $p$ ,  $t$ ,  $v$ , and  $m$  (this letter denoting the quantity of the gas without reference to its molecular condition), or if we admit the validity of the equation only between certain limits of temperature and for densities less than a certain limit of density, and also admit that between the given limits of temperature the specific heat of the gas at constant volume may be regarded as a constant quantity when the gas is sufficiently rarefied to be regarded as consisting wholly of  $\text{NO}_2$ ,—or, to speak without reference to the molecular state of the gas, when it is rarefied until its relative density  $D$  approximates to its limiting value  $D_1$ ,—we must also admit the validity (within the same limits of temperature and density) of all the calorimetrical relations which belong to ideal gas-mixtures with convertible components. The premises are evidently equivalent to this,—that we may imagine an ideal gas with convertible components such that between certain limits of temperature and above a certain limit of density the relation between  $p$ ,  $t$ , and  $v$  shall be the same for a unit of this ideal gas as for a unit of peroxide of nitrogen, and for a very great value of  $v$  (within the given limits of temperature) the thermal capacity at constant volume of the ideal and actual gases shall be the same. Let us regard  $t$  and  $v$  as independent variables; we may let these letters and  $p$  refer alike to the ideal and real gases, but we must distinguish the entropy  $\eta'$  of the ideal gas from the entropy  $\eta$  of the real gas. Now by (88)



$$\frac{d\eta}{dv} = \frac{dp}{dt}, \quad (337)$$

therefore

$$\frac{d}{dv} \frac{d\eta}{dt} = \frac{d}{dt} \frac{d\eta}{dv} = \frac{d}{dt} \frac{dp}{dt} = \frac{d^2 p}{dt^2}. \quad (338)$$

Since a similar relation will hold true for  $\eta'$ , we obtain

$$\frac{d}{dv} \frac{d\eta}{dt} = \frac{d}{dv} \frac{d\eta'}{dt}, \quad (339)$$

which must hold true within the given limits of temperature and density. Now it is granted that

$$\frac{d\eta}{dt} = \frac{d\eta'}{dt} \quad (340)$$

for very great values of  $v$  at any temperature within the given limits, (for the two members of the equation represent the thermal capacities at constant volume of the real and ideal gases divided by  $t$ ;) hence, in virtue of (339), this equation must hold true in general within the given limits of temperature and density. Again, as an equation like (337) will hold true of  $\eta'$ , we shall have

$$\frac{d\eta}{dv} = \frac{d\eta'}{dv}. \quad (341)$$

From the two last equations it is evident that in all calorimetrical relations the ideal and real gases are identical. Moreover the energy and entropy of the ideal gas are evidently so far arbitrary that we may suppose them to have the same values as in the real gas for any given values of  $t$  and  $v$ . Hence the entropies of the two gases are the same within the given limits; and on account of the necessary relation

$$d\varepsilon = t d\eta - p dv,$$

the energies of the two gases are in like manner identical. Hence the fundamental equation between the energy, entropy, volume, and quantity of matter must be the same for the ideal gas as for the actual.

We may easily form a fundamental equation for an ideal gas-mixture with convertible components, which shall relate only to the phases of equilibrium. For this purpose, we may use the equations of the form (312) to eliminate from the equation of the form (273), which expresses the relation between the pressure, the temperature, and the potentials for the proximate components, as many of the potentials as there are equations of the former kind, leaving the

potentials for those components which it is convenient to regard as the ultimate components of the gas-mixture.

In the case of a binary gas-mixture with convertible components, the components will have the same potential, which may be denoted by  $\mu$ , and the fundamental equation will be

$$p = a_1 L_1 t^{\frac{c_1 + a_1}{a_1}} e^{\frac{\mu - E_1}{a_1 t}} + a_2 L_2 t^{\frac{c_2 + a_2}{a_2}} e^{\frac{\mu - E_2}{a_2}}, \quad (342)$$

where

$$L_1 = e^{\frac{H_1 - c_1 - a_1}{a_1}}, \quad L_2 = e^{\frac{H_2 - c_2 - a_2}{a_2}}. \quad (343)$$

From this equation, by differentiation and comparison with (98), we obtain

$$\begin{aligned} \frac{\eta}{v} = L_1 \left( c_1 + a_1 - \frac{\mu - E_1}{t} \right) t^{\frac{c_1}{a_1}} e^{\frac{\mu - E_1}{a_1 t}} \\ + L_2 \left( c_2 + a_2 - \frac{\mu - E_2}{t} \right) t^{\frac{c_2}{a_2}} e^{\frac{\mu - E_2}{a_2 t}}, \end{aligned} \quad (244)$$

$$\frac{m}{v} = L_1 t^{\frac{c_1}{a_1}} e^{\frac{\mu - E_1}{a_1 t}} + L_2 t^{\frac{c_2}{a_2}} e^{\frac{\mu - E_2}{a_2 t}}. \quad (345)$$

From the general equation (93) with the preceding equations the following is easily obtained,—

$$\frac{\varepsilon}{v} = L_1 (c_1 t + E_1) t^{\frac{c_1}{a_1}} e^{\frac{\mu - E_1}{a_1 t}} + L_2 (c_2 t + E_2) t^{\frac{c_2}{a_2}} e^{\frac{\mu - E_2}{a_2 t}}. \quad (346)$$

We may obtain the relation between  $p$ ,  $t$ ,  $v$ , and  $m$  by eliminating  $\mu$  from (342) and (345). For this purpose we may proceed as follows. From (342) and (345) we obtain

$$p - a_2 t^{\frac{m}{v}} = (a_1 - a_2) L_1 t^{\frac{c_1 + a_1}{a_1}} e^{\frac{\mu - E_1}{a_1 t}} \quad (347)$$

$$a_1 t^{\frac{m}{v}} - p = (a_1 - a_2) L_2 t^{\frac{c_2 + a_2}{a_2}} e^{\frac{\mu - E_2}{a_2 t}}; \quad (348)$$

and from these equations we obtain

$$\begin{aligned} a_1 \log \left( p - a_2 t^{\frac{m}{v}} \right) - a_2 \log \left( a_1 t^{\frac{m}{v}} - p \right) = (a_1 - a_2) \log (a_1 - a_2) \\ + a_1 \log L_1 - a_2 \log L_2 + (c_2 - c_1 + a_1 - a_2) \log t - \frac{E_1 - E_2}{t}. \end{aligned} \quad (349)$$

(In the particular case when  $a_1 = 2 a_2$  this equation will be equivalent to (333)). By (347) and (348) we may easily eliminate  $\mu$  from (346).

The reader will observe that the relations thus deduced from the fundamental equation (342) without any reference to the different components of the gaseous mass are equivalent to those which relate to the phases of dissipated energy of a binary gas-mixture with components which are equivalent in substance but not convertible, except that the equations derived from (342) do not give the quantities of the proximate components, but relate solely to those properties which are capable of direct experimental verification without the aid of any theory of the constitution of the gaseous mass.

The practical application of these equations is rendered more simple by the fact that the ratio  $a_1 : a_2$  will always bear a simple relation to unity. When  $a_1$  and  $a_2$  are equal, if we write  $a$  for their common value, we shall have by (342) and (345)

$$p v = a m t, \quad (350)$$

and by (345) and (346)

$$\frac{\varepsilon}{m} = \frac{L_1(c_1 t + E_1) + L_2(c_2 t + E_2)t \frac{c_2 - c_1}{a} e^{\frac{E_1 - E_2}{at}}}{L_1 + L_2 t \frac{c_2 - c_1}{a} e^{\frac{E_1 - E_2}{at}}}. \quad (351)$$

By this equation we may calculate directly the amount of heat required to raise a given quantity of the gas from one given temperature to another at constant volume. The equation shows that the amount of heat will be independent of the volume of the gas. The heat necessary to produce a given change of temperature in the gas at constant pressure, may be found by taking the difference of the values of  $\chi$ , as defined by equation (89), for the initial and final states of the gas. From (89), (350), and (351) we obtain

$$\frac{\chi}{m} = \frac{L_1(c_1 t + at + E_1) + L_2(c_2 t + at + E_2)t \frac{c_2 - c_1}{a} e^{\frac{E_1 - E_2}{at}}}{L_1 + L_2 t \frac{c_2 - c_1}{a} e^{\frac{E_1 - E_2}{at}}}. \quad (352)$$

By differentiation of the two last equations we may obtain directly the specific heats of the gas at constant volume and at constant pressure.

The fundamental equation of an ideal ternary gas-mixture with a single relation of convertibility between its components is

$$\begin{aligned}
p = & a_1 e^{\frac{H_1 - c_1 - a_1}{a_1} \frac{c_1 + a_1}{t} \frac{\mu_1 - E_1}{e^{\frac{\mu_1 - E_1}{a_1 t}}}} \\
& + a_2 e^{\frac{H_2 - c_2 - a_2}{a_2} \frac{c_2 + a_2}{t} \frac{\mu_2 - E_2}{e^{\frac{\mu_2 - E_2}{a_2 t}}}} \\
& + a_3 e^{\frac{H_3 - c_3 - a_3}{a_3} \frac{c_3 + a_3}{t} \frac{\lambda_1 \mu_1 + \lambda_2 \mu_2 - E_3}{e^{\frac{\lambda_1 \mu_1 + \lambda_2 \mu_2 - E_3}{a_3 t}}}}, \quad (353)
\end{aligned}$$

where  $\lambda_1$  and  $\lambda_2$  have the same meaning as on page 230.

(To be continued.)

#### ERRATA.

Page 167, formula (168), for  $m_1$  read  $\mu_1$ .

" formula (169), for  $m_1, \dots, m_{n-1}$  read  $\mu_1, \dots, \mu_{n-1}$ .

Page 239, formula (333), for  $\frac{C}{t}$  read  $\frac{C}{a_2 t}$ .











